JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. *© Copyright 1971 by the American Chemical Society*

VOLUME 93, NUMBER 25 DECEMBER 15, 1971

Physical and Inorganic Chemistry

Excited-State Geometries of the Singly Substituted Methylpropenals.[1a] I. Vibrational-Electronic Analysis of $S_1(n,\pi^*)$

Robert R. Birge,* Wallace C. Pringle, and Peter A. Leermakers[1b]

Contribution from the Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457. *Received March 8, 1971*

Abstract: The vibrational-electronic band systems of the first excited n,π* singlet states of crotonaldehyde, methacrolein, and methyl vinyl ketone were investigated under low resolution. Approximately nine excited-state fundamentals were identified for each compound and compared to ground-state values obtained from infrared and far-infrared analysis. As is observed for the unsubstituted aldehyde, acrolein (see ref 2), the singly substituted methylpropenals are planar or very nearly planar in the excited state and possess considerable bond order reversal. Bond angle changes are small at all bending centers and are on the order of 3°. A comparison of selected ground- and excited-state fundamentals can be found in Table I.

The nature of the $n \rightarrow \pi^*$ transition in aldehydes and ketones is of considerable interest to both photochemists and spectroscopists. The literature has been excellently reviewed by Sidman,[3] Kasha,[4] and Turro,[5] the latter author emphasizing the photochemical nature of the n,π* state. The following two papers investigate the nature of the $n \rightarrow \pi^*$ transition in the simple α,β-unsaturated aldehyde, acrolein, and its singly substituted methyl derivatives. The discussion and experimental detail are divided into two parts; the first, which appears in this paper, presents a detailed vibrational-electronic analysis of the first excited singlet states of the four molecules, and the second, which appears in the accompanying paper,[6] uses the information afforded by the vibrational analysis in a comprehensive discussion of the excited-state geometries and the mechanisms through which the methyl groups perturb the energy of the (excited state) ψ_3 π molecular orbital and the (ground state) nonbonding electrons on oxygen. A third paper in this series will be submitted in the near future investigating the excited-state energies and geometries of the first excited triplet states.

I. Experimental Section

Acrolein (propenal), crotonaldehyde (*trans*-2-butenal), methacrolein (2-methylpropenal), and methylvinyl ketone (3-buten-2-one) were all purchased from Chemical Samples Co. Each compound was distilled three times on a 4-ft glass helices column, and the purity of the distillate checked by observation of its low-temperature (77°K) emission spectrum. Since none of the four samples emits, very small amounts of rearrangement or decomposition impurities, most of which produce a broad, structureless phosphorescence centered between 450 and 550 nm, can be detected. These impurities reappear in detectable amounts in roughly 3 days at room temperature or 1–2 weeks under refrigeration. Because of such impurities, and because acrolein and methacrolein rapidly polymerize at room temperature, compounds were distilled less than 48 hr prior to the observation of their respective spectra.

Infrared Spectra were taken on a Perkin-Elmer 621 grating infrared spectrophotometer. CsI cells (100 mm) were used in recording vapor-phase spectra in the region from 2000 to 250 cm^{-1}, and KBr cells with 0.1-mm path lengths were used in recording solution (CCl_4) spectra from 2000 to 400 cm^{-1}.

---

(1) (a) Abstracted from a portion of the Ph.D. thesis of R. R. B., Wesleyan University, 1971; (b) deceased Aug 16, 1971.

(2) J. C. D. Brand and D. G. Williamson, *Discuss. Faraday Soc.*, No. 35, 184 (1963).

(3) J. Sidman, *Chem. Rev.*, **58**, 689 (1958).

(4) M. Kasha in "Light and Life," W. B. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961.

(5) N. J. Turro, "Energy Transfer and Organic Photochemistry," P. A. Leermakers and A. Weissberger, Ed., Interscience, N. Y., 1969, pp 191–262.

(6) R. R. Birge and P. A. Leermakers, *J. Amer. Chem. Soc.*, **93**, 6726 (1971).

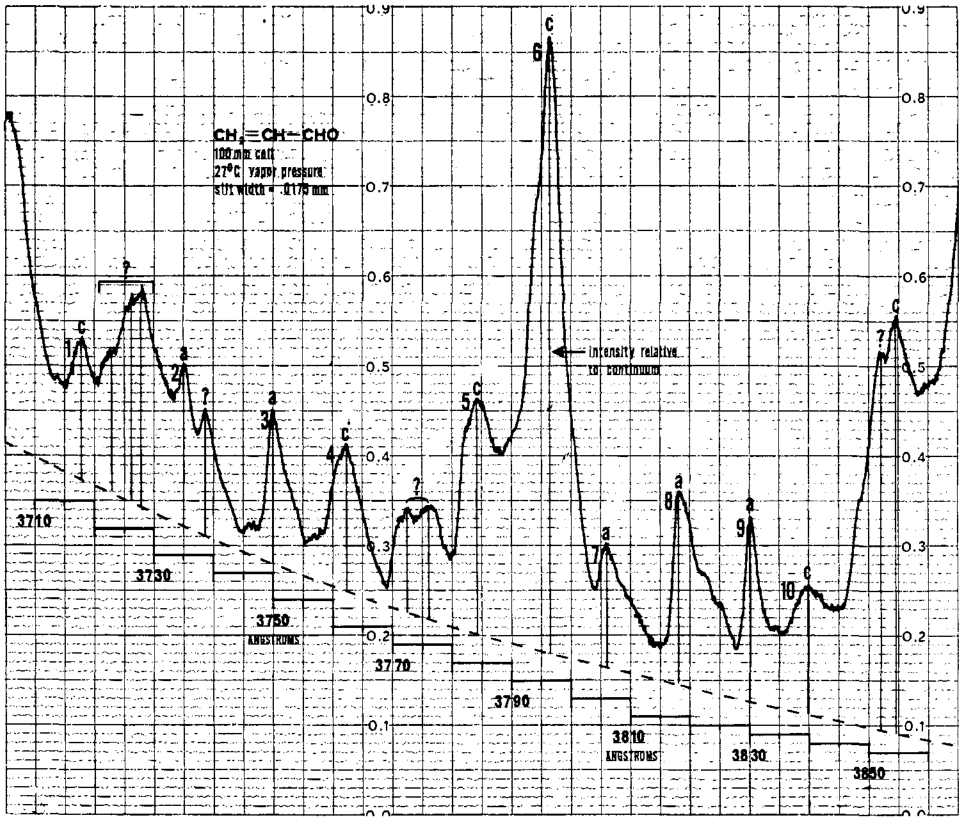

Figure 1. Band contours of acrolein vapor observed under low resolution: 1, 4, 5, 6, and 10, perpendicular bands; 2, 3, 7, 8, and 9, hybrid bands. Band 2 is the vinyl CH out-of-plane deformation, band 6 is the ∠CCO in-plane bending, band 8 is the vinyl C=C torsion, and band 9 is the skeletal torsion.

Far-infrared spectra were taken on a FS-720 RIIK Fourier spectrophotometer at room temperature using a 2-m path length. The spectra were taken from 250 to 20 cm^{-1} using BeO-ZnO filters and polyethylene windows.

Emission spectra were observed on an Aminco-Bowman spectrofluorometer at 77°K in EPA (ethyl ether–isopentane–ethanol, 5:5:2, v/v) and isopentane glasses.

Vibrational-electronic spectra were taken on a Cary 14 recording spectrophotometer, the electronics adjusted to produce an optimized amplifier sensitivity with a response damping time constant of approximately 1 sec. These adjustments permitted the use of slit widths on the order of 0.0075–0.0200 mm (spectral band widths = 0.3–1.0 Å), taking maximum advantage of the dispersion of the double monochromator.

A typical spectrum is reproduced in Figure 1. Because of the sharpness of the peaks, band maxima could usually be assigned with a reproducibility of better than ±0.2 Å. Benzene vapor and formaldehyde vapor were used to calibrate the spectra.

Vapor-phase spectra were taken at several pressures in standard all-quartz cells of various path lengths as well as a 100-mm quartz cell which was wound with resistance wire and could be heated electrically. The cell was designed so that the cell ends could be held at a higher temperature than the main body to prevent condensation on the windows. Spectra were observed at temperatures ranging from 25 to about 200° to assist in assignment of hot bands and to determine the position of the vibrational origin.

II. Results and Discussion

(A) Vibrational-Electronic Spectra. The first excited singlet electronic band systems of acrolein and its three singly substituted methylated derivatives commence near 3900 Å. The absorption spectra, when observed in solution, exhibit characteristics associated with n → π* transitions:[3] low molar absorptivity ($\epsilon < 20$), blue shift on methylation, and red shift on changing solvent environment from polar (ethanol) to nonpolar (cyclohexane).

Acrolein,[7a] crotonaldehyde,[7b] and methacrolein[8] exist

Table I. Selected Ground- and Excited-State Fundamentals and System Origins of the Singly Substituted Methylpropenals

Assignment	$CH_2{=}CHCHO$[a]		$CH_3CH{=}CHCHO$		$CH_2{=}C(CH_3)CHO$		$CH_2{=}CHCOCH_3$	
0, 0 ($S_0 \rightarrow S_1(n,\pi^*)$)	25,861 cm^{-1} 73.94 kcal		26,497 cm^{-1} 75.76 kcal		26,492 cm^{-1} 75.75 kcal		26,123 cm^{-1} 74.69 kcal	
	Fundamentals, cm^{-1}							
	ω''	ω'	ω''	ω'	ω''	ω'	ω''	ω'
C=O stretch (a′)	1723	1266	1720	1238	1717	1222	1724	1191
C=C stretch (a′)	1625	1410	1644	1363	1645	1320	1630	1305
∠CCO bending (a′)	564	488	537	457	630	535	490	381
Skeletal torsion (a″)	158	250	206	243	163	233	101	230

[a] See ref 2.

---

[7] (a) R. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, *J. Chem. Phys.*, **26**, 634 (1957); E. A. Cherniak and C. C. Costain, *ibid.*, **45**, 104 (1966); (b) H. Mackle and L. E. Sutton, *Trans. Faraday*

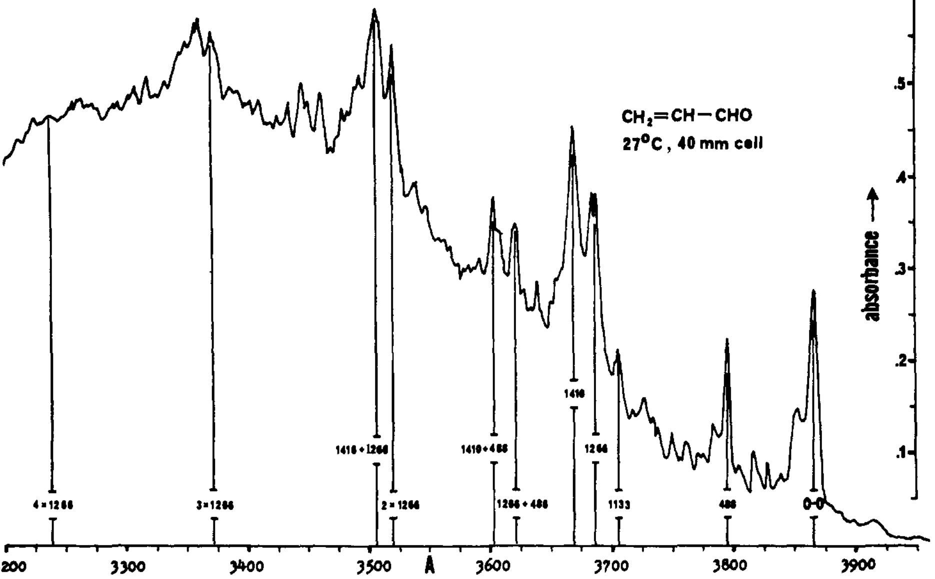

Figure 2. Low-resolution spectrum of the first excited singlet of acrolein.

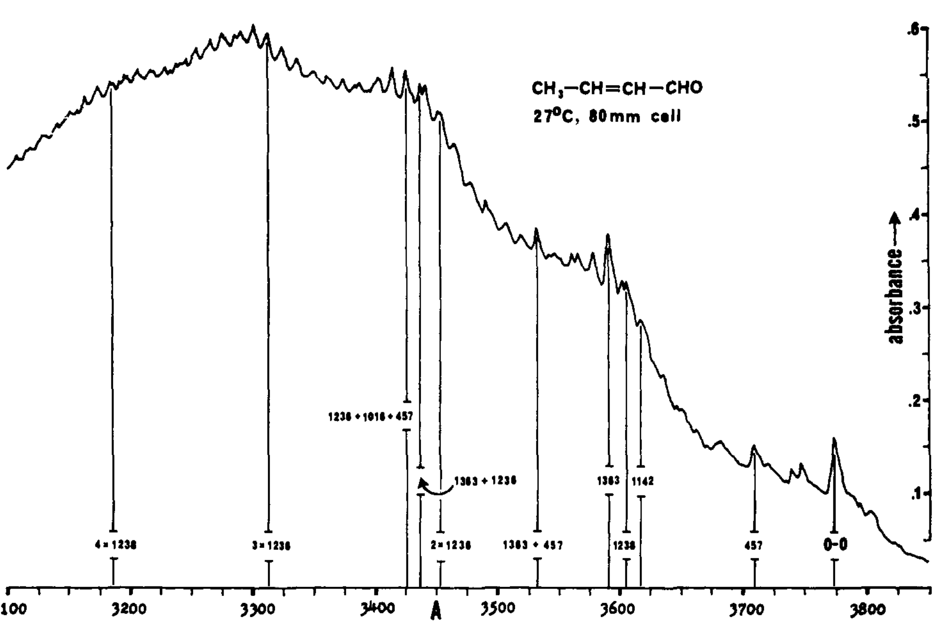

Figure 3. Low-resolution spectrum of the first excited singlet of crotonaldehyde.

almost entirely in the planar s-trans configuration. Methyl vinyl ketone, however, possesses two stable conformations at room temperature,[9] but the only configuration contributing to the vibrational fine structure of the electronic spectrum appears to be the s-trans (see section II.A.4). These similarities in molecular configuration and symmetry (C_s point group) result in a high degree of similarity in vibronic activity. Each compound will be discussed separately.

(1) Acrolein. The vibrational-electronic spectrum of the first excited singlet of acrolein has been extensively studied under both high and low resolution, most recently by Hollas[10] and Brand and Williamson.[2] The latter authors provided a thorough analysis of the excited-state fundamentals which was most helpful in analyzing the singly substituted methyl derivatives. The salient features of the electronic spectrum of acrolein will be briefly discussed.

The system origin (0–0 band) and the principal fundamentals of the vibronic spectrum of acrolein are perpendicular bands of a near-symmetric top. The treatment of rotational fine structure requires the assignment of prominent perpendicular vibronic bands to totally symmetrical fundamentals, indicating that the electronic transition is polarized perpendicular to the molecular plane ($A'' \leftarrow A'$).[2] These observations are consistent with the excitation of one of the nonbonding electrons of oxygen into the mobile π lattice (*i.e.*, $n \rightarrow \pi^*$ transition).

The vibrations of a molecule possessing C_s symmetry can be classified as either totally symmetrical (vibra-

---

Soc., 47, 691 (1951); M. Suzuki and K. Kozima, *Bull. Chem. Soc. Jap.*, 42, 2183 (1969).

[8] W. G. Fateley, R. K. Harris, F. A. Miller, and R. E. Witkowski, *Spectrochim. Acta*, 21, 231 (1965).

[9] K. Noack and R. N. Jones, *Can. J. Chem.*, 39, 2225 (1961).

[10] J. M. Hollas, *Spectrochim. Acta*, 19, 1425 (1963).

Table II. Principal Assignments in the 3774-Å System of Crotonaldehyde

Cm$^{-1\,a}$		Intensity^{b}	Assignment
25,595	−902		8(−206) + 3(243) = −919
25,859	−638		3(−206) = −618
25,980	−517		6(−206) + 3(243) = −507
26,082	−415		2(−206) = −412
26,202	−295		5(−206) + 3(243) = −301
26,291	−206	2	−206 (skeletal torsion)
26,406	−91	2	4(−206) + 3(243) = −95
26,497	0	10	Origin
26,567	70	1	2(243) + 2(−206) = 74
26,621	124	2	2(243) + 2(−206) + 187 − 140 = 121
26,684	187	4	187 (methyl torsion)
26,740	243	3	243 (skeletal torsion)
26,813	316	2	316 (3(243) + 2(−206) = 317)
26,872	375	3	375 (vinyl C=C torsion)
26,954	457	5	457 (∠CCO in plane bending)
27,170	673	3	673 (formyl CH out-of-plane deform)
27,307	810	2	1019 − 206 = 813
27,414	917	2	673 + 243 = 916
27,516	1019	3	1019 (vinyl CH in-plane deform)
27,639	1142	4	1142 (formyl CH in-plane deform)
27,735	1238	5	1238 (carbonyl stretch)
27,757	1260	5	2(673) in Fermi resonance with 1238
27,860	1363	8	1363 (C=C stretch)
27,952	1455	4	1455 (methyl asym bending)
28,043	1546	2	1363 + 187 = 1550
28,093	1596	2	1142 + 457 = 1599
28,316	1819	5	1363 + 457 = 1820
28,413	1916	3	1455 + 457 = 1912
28,525	2028	2	1363 + 673 = 2036
28,647	2150	3	1238 + 673 + 243 = 2154
28,756	2259	3	1238 + 1019 = 2257
28,862	2365	4	1238 + 457 + 673 = 2368
28,975	2478	4	2(1238) = 2476
29,073	2576	4	1238 + 1019 + 316 = 2573
29,110	2613	4	1238 + 1363 = 2601
29,201	2704	5	1238 + 1019 + 457 = 2714
29,292	2795	5	1238 + 1363 + 187 = 2788
29,390	2893	4	1238 + 1019 + 457 + 187 = 2901
29,537	3040	3	1363 + 1238 + 243 + 187 = 3031
29,651	3154	3	2(1238) + 673 = 3149
29,751	3254	3	1363 + 1238 + 457 + 187 = 3245
29,855	3358	3	1363 + 1238 + 316 + 243 + 187 = 3347
29,978	3481	3	1455 + 1363 + 673 = 3491
30,083	3586	3	1238 + 1142 + 1019 + 187 = 3586
30,188	3691	3	3(1238) = 3714
30,289	3792	4	2(1238) + 673 + 457 + 187 = 3793
30,399	3902	3	3(1238) + 187 = 3901
30,487	3990	2	2(1238) + 673 + 457 + 375 = 3981
30,527	4030	3	2(1238) + 673 + 457 + 243 + 187 = 4036
30,743	4246	3	2(1238) + 673 + 2(457) + 187 = 4250
30,848	4351	2	3(1238) + 457 + 187 = 4358
30,964	4467	2	2(1238) + 2(673) + 457 + 187 = 4466
31,068	4571	2	3(1238) + 673 + 187 = 4574
31,176	4679	3	3(1238) + 457 + 316 + 187 = 4674

[a] *In vacuo.* [b] Intensity of discrete bands relative to continuum. $I_{00}/(I_{00} + \Sigma_i I_{v_i(01)}) = 0.19$, $I_{00}/(I_{00} + I_{\angle CCO}) = 0.67$.

tions remain within the molecular plane) or nontotally symmetrical (vibrations have at least one component directed out of the molecular plane). The most prominent fundamentals of the excited state involve the totally symmetrical vibrations of the vinyl C=C and carbonyl stretching and the in-plane bending of the CCO moiety. These bands occur at 1410, 1266, and 488 cm^{-1}, respectively.[2] A less prominent totally symmetrical fundamental is found at 1133 cm^{-1} and is assigned to the in-plane deformation of the formyl CH bond.[2] The 1266-cm^{-1} fundamental forms the main progression and can be observed up to its third overtone. These bands are all designated in Figure 2.

In addition to the four totally symmetrical fundamentals, five parallel bands associated with nontotally symmetrical fundamentals are found at 909 (vinyl CH "wag"), 644 (formyl CH out-of-plane deformation), 582 (vinyl CH$_2$ out-of-plane deformation), 333 (vinyl C=C torsion), and 250 cm^{-1} (skeletal torsion).[2]

The rotational fine structure of the perpendicular bands exhibits a symmetrical intensity distribution on both sides of the central maximum when viewed under low resolution. This "macro" symmetry is in observable contrast to the contours of most of the hybrid bands which gradually degrade to the red but sharply drop off to the blue. These differences are demonstrated in Figure 1, which shows a portion of the vibronic spectrum of acrolein. Perpendicular bands are designated with a small c, while hybrid parallel bands are indicated with a small a (the letter a was chosen to indicate that these bands are largely type A in polarization[2]). Band contours of the low-resolution vibronic spectra were helpful in the assignment of the singly substituted methylpropenals.

A more comprehensive discussion of acrolein can be found in ref 2 and 10.

(2) Crotonaldehyde. The low-resolution spectrum of the first excited singlet state of crotonaldehyde is shown in Figure 3. The vibrational band structure is well defined at longer wavelengths (3150–3800 Å), but merges into the continuum at shorter wavelengths. The continuum reaches a maximum at approximately 3300 Å. An analysis of the main progression and the hot bands indicates that the strong band at 26,497 cm^{-1} is the origin of the transition to the first excited singlet (Table II). (In C_s symmetry, the 0–0 transition is formally allowed and would be expected to be a comparatively strong band.) Seven relatively weak hot bands were resolved to the red of the system origin, only one of which appears to be a fundamental. This band occurs at 206 cm^{-1} and is assigned to the ground-state skeletal torsion. The remaining six bands involve overtones of this fundamental or combinations of this fundamental with the excited-state skeletal torsion at 243 cm^{-1}.

More than 85 bands are clearly visible to the blue of the origin, the more prominent of which are assigned in Table II. All of the observed fundamentals could be classified as to polarity through observation of their band contour (see section 1), intensity, frequency, or participation in combinations with other bands of known polarity.

Four strong bands at 457, 1142, 1238, and 1363 cm^{-1} are assigned to totally symmetrical fundamentals. The lowest frequency band is assigned to the in-plane bending of the CCO moiety. This fundamental corresponds closely in wavenumber to the ∠CCO bending in acrolein which occurs at 488 cm^{-1}. The fractional intensity of the system origin relative to these bending modes (calculated as the ratio of the 0–0 band intensity to the sum of the 0–0 band and the bending band intensities; see bottom of Table II) provides a quantitative estimate of the change in angle at the respective bending center upon excitation. The value for crotonaldehyde (0.67; see Table II) is very simi-

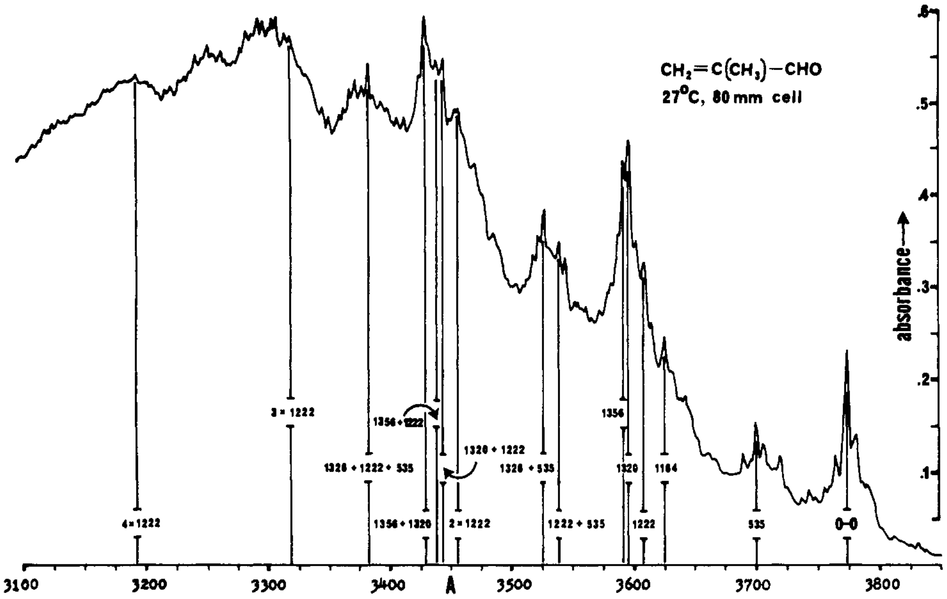

Figure 4. Low-resolution spectrum of the first excited singlet of methacrolein.

lar to the value calculated for acrolein (0.60) using the data of Brand and Williamson.[2] This indicates that bond angle changes are approximately the same for both molecules, *i.e.*, the CCO angle increases by roughly 3°.[10]

The band at 1019 cm^{-1} can be assigned to either an in-plane or out-of-plane vinylic hydrogen deformation. We tentatively prefer the former assignment because of the unusually strong interaction of this vibration with the totally symmetrical $\angle$CCO in-plane bending and carbonyl stretching vibrations to form the strong band at 2704 cm^{-1} (see Table II).

The perpendicular band at 1142 cm^{-1} can be assigned to the in-plane deformation of the formyl hydrogen. This fundamental is found at 1133 cm^{-1} in acrolein. Since the methyl group in crotonaldehyde is separated from the formyl group by two carbons, the similarity in wavenumber for the two molecules is not unexpected.

The strong perpendicular bands at 1238 and 1363 are assigned to the excited-state stretching of the carbonyl and the C=C bonds, respectively. The 1238-cm^{-1} vibration forms the main progression and is doubled in its first quantum transition by Fermi resonance with the 673-cm^{-1} fundamental. The 1363-cm^{-1} fundamental, however, does not appear in any overtones, despite the fact that elementary Franck–Condon considerations would indicate that this vibration should have a strong 0–2 and 0–3 band. The lack of such a progression indicates that this stretching mode is strongly coupled with the central C—C bond, creating an overall antisymmetrical motion, as was observed for the C=C stretching in acrolein.[2]

In addition to the five totally symmetrical fundamentals, five additional bands associated with nontotally symmetrical fundamentals are found at 187, 243, 375, 673, and 1455 cm^{-1}. The bands at 187, 243, and 375 can all be assigned to torsional vibrations of the excited state. The strong interaction of the 243-cm^{-1} fundamental with the hot-band fundamental at 206 cm^{-1} directs the assignment of this vibration to the excited-state skeletal torsion. The band at 187 cm^{-1} is probably the methyl torsion, since it is much too low in frequency to be the vinyl C=C torsion.[11] The ground-state methyl torsion is found at 140 cm^{-1} (section II.B), which indicates that the methyl torsion increases more upon excitation than does the skeletal torsion (43 cm^{-1} *vs.* 37 cm^{-1}). The observation that the 187-cm^{-1} fundamental is stronger than the 243-cm^{-1} band, indicating a higher electron density change at the bond associated with the 187-cm^{-1} torsion, lends support to our assignments. The observation of an increase in methyl torsion on excitation is significant and indicates that excited-state resonant interaction of the methyl group with the mobile π system ("hyperconjugation") is occurring to increase the bond order reversal. The quantitative aspects of this interaction will be discussed in greater detail in the accompanying paper.[6] The remaining torsional fundamental at 375 cm^{-1} is assigned to the vinyl C=C torsion.

The band at 673 cm^{-1} can be assigned, by analogy to acrolein, to the formyl CH out-of-plane hydrogen deformation. The remaining nontotally symmetrical fundamental at 1455 cm^{-1} must be associated with the methyl group, since it is much too high in frequency to be associated with any out-of-plane hydrogen deformation of the vinyl or formyl group. Because of its hybrid character, this fundamental is assigned to the asymmetric bending of the methyl group hydrogens. The surprising intensity of this band is probably associated more with interaction with the C=C stretching than with any Franck–Condon effect associated with

---

(11) Throughout this paper the term "vinyl" will be used to represent both the unsubstituted (*e.g.*, acrolein and methyl vinyl ketone) and substituted (*e.g.*, crotonaldehyde and methacrolein) olefinic moiety.

Table III. Principal Assignments in the 3775-Å System of Methacrolein

Cm^{-1}[a]		Intensity[b]	Assignment
25,859	−633	3	−633 (∠CCO in-plane bending)
25,966	−526	1	2(−268) = −536
26,047	−445	1	7(−163) + 3(233) = −442
26,115	−373	1	8(−163) + 4(233) = −372
26,224	−268	2	−268 (in-plane bending[c])
26,287	−205	3	7(−163) + 4(233) = −209
26,372	−120	10	5(−163) + 3(233) = −116
26,405	−87	10	2(−163) + 233 = −93[c]
26,443	−49	18	6(−163) + 4(233) = −46
26,492	0	30	Origin
26,564	72	11	233 − 163 = 70
26,599	107	5	4(233) + 5(−163) = 117[c]
26,632	140	4	2(233) + 2(−163) = 140
26,675	183	2	183 (methyl torsion)
26,725	233	2	233 (skeletal torsion)
26,755	263	2	183 + 233 − 163 = 253
26,792	300	2	2(233) − 163 = 303
26,834	342	5	394 + 6(−163) + 4(233) = 348
26,886	394	10	394 (vinyl C=C torsion)
26,905	413	8	535 + 3(233) + 5(−163) = 419
26,987	495	13	535 + 4(233) + 6(−163) = 489
27,027	535	17	535 (∠CCO in-plane bending)
27,059	567	5	567 (vinyl CH_2 out-of-plane deform)
27,102	610	6	535 + 233 − 163 = 605
27,137	645	2	567 + 233 − 163 = 637
27,220	728	1	535 + 183 = 718
27,281	789	2	535 + 183 + 233 − 163 = 788
27,317	825	2	567 + 183 + 233 − 163 = 820
27,386	894	3	1104 + 4(233) + 7(−163) = 895
27,431	939	5	535 + 394 = 929
27,453	961	6	567 + 394 = 961
27,483	991	7	1104 + 3(233) + 5(−163) = 988
27,540	1048	9	1104 + 4(233) + 6(−163) = 1058
27,596	1104	14	1104 (formyl CH in-plane deform)
27,666	1174	12	1222 + 4(233) + 6(−163) = 1176
27,714	1222	22	1222 (carbonyl stretch)
27,765	1273	25	1320 + 4(233) + 6(−163) = 1274
27,812	1320	40	1320 (C=C stretch)
27,848	1356	37	1356 (methyl sym bending)
27,878	1386	22	1320 + 233 − 163 = 1390
27,992	1430	13	1356 + 233 − 163 = 1426
27,949	1457	10	1457 (methyl asym bending)
27,987	1495	6	1104 + 394 = 1498
28,077	1585	4	1356 + 233 = 1589
28,137	1645	5	1104 + 535 = 1939
28,212	1720	10	1320 + 394 = 1714
28,252	1760	12	1222 + 535 = 1757
28,309	1817	10	1356 + 394 + 233 − 163 = 1820
28,356	1864	18	1320 + 535 = 1855
28,388	1896	10	1356 + 535 = 1891
28,424	1932	6	1320 + 535 + 233 − 163 = 1925
28,533	2041	4	1320 + 535 + 183 = 2038
28,694	2202	6	2(1104) = 2208
28,762	2270	11	1222 + 1104 + 4(233) − 6(−163) = 2280
28,818	2326	13	1222 + 1104 = 2326
28,930	2438	18	2(1222) = 2444
28,954	2462	17	1356 + 1104 = 2460
28,987	2495	16	1320 + 1222 +4(233) + 6(−163) = 2496
29,033	2541	26	1320 + 1222 = 2542
29,073	2581	25	1356 + 1222 = 2578
29,137	2645	25	2(1320) = 2640
29,166	2674	29	1356 + 1320 = 2676
29,303	2811	7	1457 + 1356 = 2813
29,351	2859	7	1222 + 1104 + 535 = 2861
29,456	2964	10	1320 + 1104 + 535 = 2959
29,563	3071	15	1320 + 1222 + 535 = 3077
29,614	3122	10	1356 + 1222 + 535 = 3113
29,668	3176	11	2(1320) + 535 = 3175
29,696	3204	10	1356 + 1320 + 535 = 3211
30,162	3670	19	3(1222) = 3666
30,243	3751	21	2(1320) + 1104 = 3744
30,379	3887	19	1356 + 1320 + 1222 = 3898
30,454	3962	16	3(1320) = 3960
30,698	4206	10	3(1222) + 535 = 4201
30,769	4277	11	2(1320) + 1104 + 535 = 4279

[a] *In vacuo.* [b] Intensity of discrete bands relative to continuum. $I_{00}/(I_{00} + \Sigma_i I_{v_i(01)}) = 0.13$. $I_{00}/(I_{00} + I_{\angle CCO}) = 0.64$. [c] An alternate assignment is discussed in the text.

geometrical changes in the bond angles or force constants within the methyl group.

The relatively intense system origin, the lack of out-of-plane bending modes, and the observation that the central C–C bond experiences a large increase in electron density indicates that the excited-state singlet is planar, or very nearly planar, and possesses considerable bond order reversal. The fractional intensity of the system origin in crotonaldehyde (calculated as the ratio of the 0–0 band intensity to the sum of the intensities of all the fundamentals in their first quantum transitions (including 0–0 band)) is 0.19, as compared to 0.21 in acrolein, and indicates that the overall geometry change upon excitation is greater for crotonaldehyde than for acrolein.

(3) Methacrolein. The vibronic spectrum of methacrolein is shown in Figure 4 and assigned in Table III. The vibrational fine structure is comparatively complex and consists of sharp bands which are well defined on the long-wavelength side (3200–3800 Å), eventually merging into the continuum at shorter wavelengths. The continuum reaches a maximum at roughly the same wavelength as crotonaldehyde (3300 Å). An analysis of the hot bands and the main and secondary progressions indicates that the strong band at 26,492 cm^{-1} is the system origin. Of the ten surprisingly intense hot bands, two appear to be fundamentals, one involving an in-plane bending at 268 cm^{-1} (ir band at 268 cm^{-1}, section II.B) and the second involving the in-plane bending of the CCO moiety at 633 cm^{-1} (ir band at 630 cm^{-1}). The skeletal torsion fundamental is apparently hidden under the intense combination bands involving the interaction of the ground-state (163 cm^{-1}, see section II.B) and excited-state (233 cm^{-1}) skeletal torsions. Nine such bands are encountered in the spectrum, six to the red and three to the blue of the 0–0 band.

Approximately 100 bands were resolved to the blue side of the origin, the more prominent of which are assigned in Table III. All of the ten observed fundamentals discussed below are assigned with reasonable confidence as to vibrational symmetry.

A total of five bands associated with totally symmetrical fundamentals are found at 535, 1104, 1222, 1320, and 1356 cm^{-1}. The low-frequency vibration at 535 cm^{-1} is assigned to the ∠CCO in-plane bending mode and exhibits a fractional intensity relative to the system origin of 0.64 as compared to 0.67 for crotonaldehyde and 0.60 for acrolein. Consequently, the bond angle change at this bending center is analogous for the three molecules and is on the order of 3°.[10]

The perpendicular band at 1104 cm^{-1} is in the region expected for inplane hydrogen deformation and because of its intensity is assigned to the formyl CH in-plane deformation. Brand and Williamson[2] have determined that the intensity of this deformation in acrolein is due primarily to intensity borrowing from the excited-state carbonyl stretching, an especially efficient interaction due to the similarities in frequency.

The strong bands at 1222 and 1320 cm^{-1} are assigned to the excited-state stretching of the carbonyl and C=C groups, respectively. The 1222-cm^{-1} fundamental forms the main progression and is observed through to the fourth quantum transition, while the 1320-cm^{-1} fundamental forms a subprogression which is active to the third quantum transition. Unlike acrolein, crotonaldehyde, and methyl vinyl ketone (see next section), the C=C stretching does not appear to have any antisymmetrical character. This would indicate that the central C–C and C–CH$_3$ stretching vibrations are mixing to an equivalent degree with the 1320-cm^{-1} fundamental, thereby producing a symmetrical interaction.

The perpendicular band of highest frequency is found at 1356 cm^{-1} and is assigned to the symmetrical bending of the methyl hydrogens. The high intensity of this vibration must be due to efficient intensity borrowing, the most likely source being the C=C stretching.

Five hybrid bands associated with nontotally symmetrical fundamentals are found at 183, 233, 394, 567, and 1457 cm^{-1}. The first three bands are assigned, in analogy to crotonaldehyde, to the methyl, skeletal, and C=C torsions of the excited state. As was found for the crotonaldehyde spectrum, the ground- and excited-state skeletal torsions interact strongly to produce a number of combination bands. Unfortunately, no hot band could be unequivocably assigned to a combination of ground-state and excited-state methyl torsions, though the combination bands at −87 and 107 cm^{-1} are good candidates, since they do not appear to follow the general sequence found for most of the skeletal torsion combination bands. Hypothesizing that these two bands do involve the methyl torsions, a value for the ground-state torsion can be numerically set at either 132 or 264 cm^{-1}. Appropriate assignments would be as follows.

Distance from origin	Ground state 132	Ground state 264
−87 cm^{-1}	2(−132) + 183 = −81	−264 + 183 = −81
107 cm^{-1}	2(−132) + 2(183) = 102	−264 + 2(183) = 102

Since these bands can also be assigned as combinations of ground-state and excited-state skeletal torsions (Table III), the above assignments should not be given too much weight. The intensity of the 183-cm^{-1} fundamental does indicate, however, that the torsional change on excitation is quantitatively similar to that found for crotonaldehyde.

The fundamental at 567 cm^{-1} must be associated with the out-of-plane deformation of either the vinyl CH$_2$ or formyl CH group. Since the fundamental interacts strongly with the C=C double bond (to produce a medium-intensity band at 28,388 cm^{-1}), but not at all with the carbonyl group, the former assignment is more likely.

Table IV. Principal Assignments in the 3828-Å System of Methyl Vinyl Ketone

Cm^{-1}[a]		Intensity[b]	Assignment
25,624	−499	vw	−499 (∠CCO in-plane bending)
25,714	−409	vw	5(−111) + 147 = −408
25,769	−354	vw	8(−101) + 2(230) = −348
25,880	−243	vw	7(−101) + 2(230) = −247
25,949	−174	vw	4(−101) + 230 = −174
26,012	−111	m	−111 (methyl torsion)
26,048	−75	mw	2(−111) + 147 = −75
26,082	−41	mw	3(−111) + 2(147) = −39
26,123	0	s	Origin
26,158	35	s	147 − 111 = 36
26,229	106	w	3(147) + 3(−111) = 108
26,270	147	mw	147 (methyl torsion)
26,353	230	mw	230 (skeletal torsion)
26,390	267	mw	230 + 147 − 111 = 266
26,466	343	m	381 + 2(147) + 3(−111) = 342
26,504	381	s	381 (∠CCO in-plane bending)
26,539	416	m	381 + 147 − 111 = 417
26,610	487	w	381 + 3(147) + 3(−111) = 489
26,645	522	w	381 + 4(147) + 4(−111) = 525
26,730	607	w	607 (vinyl CH$_2$ out-of-plane deform)
26,767	644	w	607 + 147 − 111 = 643
26,838	715	w	607 + 3(147) + 3(−111) = 715
26,878	755	w	607 + 4(147) + 4(−111) = 751
27,063	940	w	940 (vinyl CH in-plane deform)
27,218	1095	w	607 + 381 + 3(147) + 3(−111) = 1096
27,314	1191	m	1191 (carbonyl stretch)
27,353	1230	w	1191 + 147 − 111 = 1227
27,428	1305	s	1305 (C=C stretch)
27,464	1341	s	1305 + 147 − 111 = 1341
27,583	1460	ss	1460 (methyl asym bending)
27,696	1573	m	1191 + 381 = 1572
27,804	1681	m	1191 + 381 + 3(147) + 3(−111) = 1680
27,886	1763	m	1191 + 381 + 230 + 2(147) + 3(−111) = 1763
27,925	1802	m	1191 + 381 + 230 = 1802
28,030	1907	mw	1191 + 607 + 3(147) + 3(−111) = 1906
28,066	1943	mw	1191 + 607 + 147 = 1938
28,185	2062	w	1460 + 607 = 2067
28,300	2177	w	1460 + 607 + 3(147) + 3(−111) = 2175
28,375	2252	w	1305 + 940 = 2245
28,401	2278	w	1305 + 940 + 147 − 111 = 2281
28,496	2373	m	2(1191) = 2382
28,542	2419	w	2(1191) + 147 − 111 = 2418
28,645	2522	m	2(1191) + 147 = 2529
28,764	2641	ms	1460 + 1191 = 2651
28,880	2757	s	2(1191) + 381 = 2763
28,998	2875	s	1305 + 1191 + 381 = 2877
29,121	2998	m	2(1191) + 381 + 230 = 2993
29,231	3108	w	1305 + 1191 + 381 + 230 = 3107
29,348	3225	w	2(1191) + 607 + 230 = 3219
29,560	3437	w	1305 + 1191 + 940 = 3436
29,695	3572	w	3(1191) = 3573
29,819	3696	w	2(1191) + 1305 = 3687

[a] *In vacuo.* [b] Intensity of discrete bands relative to continuum; vw = very weak, w = weak, m = medium, s = strong. $I_{00}/(I_{00} + \Sigma_i I_{v_i(01)}) \cong 0.2$. $I_{00}/(I_{00} + I_{\angle CCO}) \cong 0.5$.

The fundamental at 1457 cm^{-1} is assigned to the asymmetric methyl bending, in analogy to crotonaldehyde. The vibration is found to increase only slightly from 1455 to 1457 cm^{-1} on excitation.

The strong system origin, the lack of out-of-plane bending modes, and the increase in the skeletal torsion coupled with a large decrease in the carbonyl and C=C stretching frequencies indicate that a significant amount of bond order reversal takes place and that the excited state is planar, or very nearly planar. The fractional

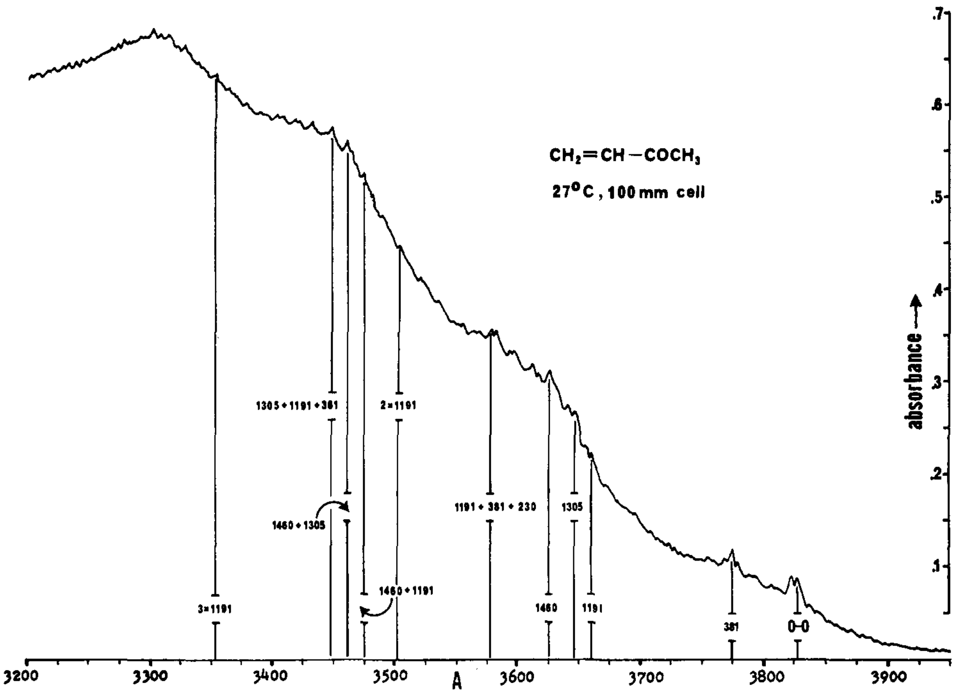

Figure 5. Low-resolution spectrum of the first excited singlet of methyl vinyl ketone.

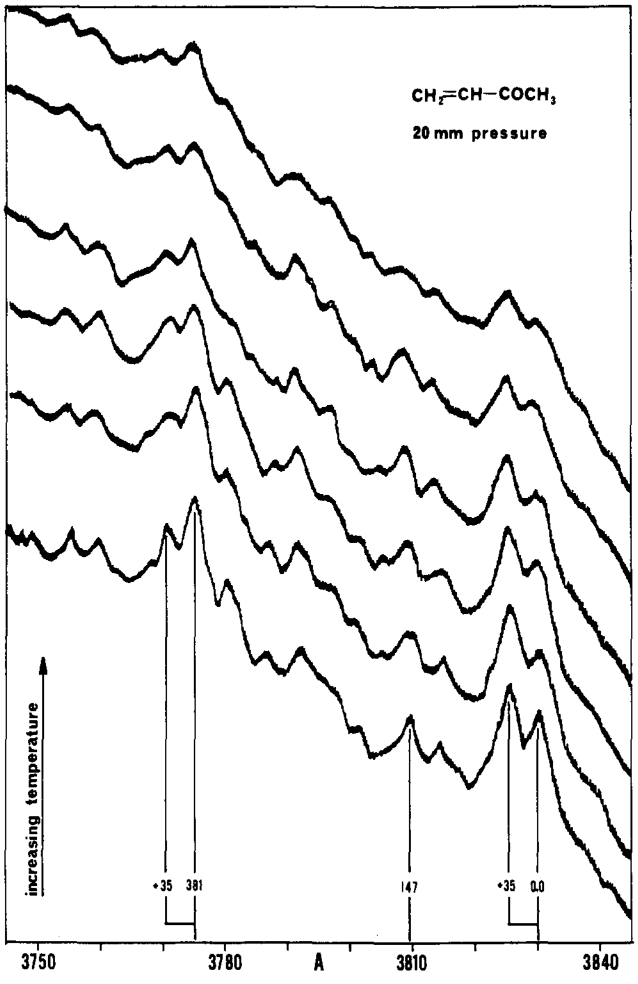

Figure 6. The effect of temperature on the band system of methyl vinyl ketone.

intensity of the system origin is 0.13 (Table III), indicating that the geometry change is greater for methacrolein than for either acrolein or crotonaldehyde.

(4) Methyl Vinyl Ketone. The low-resolution spectrum of methyl vinyl ketone is shown in Figure 5. The vibrational fine structure, which appears on the long-wavelength side of the continuum, is less well defined for this compound than for the three aldehydes and complicates vibrational analysis. The continuum reaches a maximum at approximately 3320 Å. The vibrational analysis of the hot bands and the carbonyl progression indicates that the system origin is the relatively strong band at 26,123 cm^{-1} (see Table IV). Of the eight resolvable bands to the red of the system origin, only two appear to be associated with ground-state fundamentals. A medium-strength band at 111 cm^{-1} is assigned to the ground-state methyl torsion because of its strong interaction with the corresponding excited-state fundamental. The skeletal torsion, which should appear at 101 cm^{-1} (see section II.B), is apparently hidden under the more vibronically active methyl torsion band, but is observed to participate in three combination (hot) bands at −174, −243, and −354 cm^{-1}. The very weak band at 499 cm^{-1} (ir band at 490 cm^{-1}) is assigned to the ∠CCO in-plane bending.

More than 70 bands were resolved to the blue of the system origin, the more prominent of which are assigned in Table IV. All of the bands appear to be associated entirely with the s-trans configuration, because (1) increasing the temperature at constant vapor pressure raises the level of the continuum relative to the discrete band structure (see Figure 6) and (2) the excited-state carbonyl stretching frequency can only be associated with the s-trans ground-state carbonyl frequency as determined by Franck–Condon intensity distribution calculations on the carbonyl vibronic progression (see accompanying paper[6]). In support of our observation, a microwave investigation of methyl vinyl ketone indicated that the percentage of s-cis present at room temperature is actually quite small.[12]

The four bands at 381, 940, 1191, and 1305 cm^{-1} are assigned to totally symmetrical fundamentals. The low-frequency fundamental at 381 cm^{-1} is assigned to the ∠CCO in-plane bending and exhibits a fractional intensity of approximately 0.50, indicating that the bond angle change at this bending center is similar to that found for acrolein (about 3° [11]).

The band at 940 cm^{-1} was too weak to be assigned polarity using band contour, but on the basis of intensity and frequency is tentatively assigned to the totally symmetrical in-plane deformation of the vinyl CH. This assignment corresponds well with the analogous assignment in crotonaldehyde in which the vinyl CH in-plane deformation is both weak and decreases in frequency on excitation, 21.9% *vs.* 24.8% in methyl vinyl ketone. Furthermore, the percentage difference in going from crotonaldehyde to methyl vinyl ketone (24.8 − 21.9 = 2.9%) is quantitatively similar to the comparative C=C stretching frequency change in the two molecules, which decreases 17.1% on excitation in crotonaldehyde and 19.9% in methyl vinyl ketone (19.9 − 17.1 = 2.8%). Since both the in-plane CH deformation and C=C stretch are totally symmetrical and affected in a similar direction by vinylic electron density, the percentage differential would be expected to be similar. The remarkable similarity, however, is probably fortuitous.

The totally symmetrical fundamentals at 1191 and 1305 cm^{-1} are assigned to the excited-state carbonyl and C=C stretching, respectively. The 1191-cm^{-1} vibration forms the main progression and is observed through the third quantum transition; the continuum apparently obscures the 0–4 transition. The 1305-cm^{-1} fundamental appears in only the first quantum transition, indicating an antisymmetrical coupling of the vinylic and central C–C stretching vibrations, as was observed for both acrolein and crotonaldehyde.

Four bands associated with nontotally symmetrical fundamentals are found at 147, 230, 607, and 1460 cm^{-1}. The 147-cm^{-1} fundamental interacts strongly with a ground-state fundamental at 111 cm^{-1} to produce a series of combination bands, the strongest of which is the 35-cm^{-1} band produced by the singly quantized interaction of the two vibrations (147 − 111 = 36 cm^{-1}). This particular combination band adds to almost all of the fundamentals with the notable exception of the strong 1460-cm^{-1} vibration. The latter fundamental is assigned to the asymmetric methyl torsion and indicates, possibly, that the local symmetry of the methyl group is active in preventing normal-coordinate interaction. The 147-cm^{-1} fundamental is assigned to the excited-state methyl torsion for three reasons: (1) the ground-state 111-cm^{-1} frequency is obscured in the far-infrared spectrum by a stronger band which has been assigned to the skeletal torsion (see section II.B), (2) the frequency change on excitation (32.4% increase) is analogous to that found for the methyl torsion in crotonaldehyde (33.5%), and (3) the excited-state frequency is in the region expected for methyl torsions attached to carbonyl groups (acetaldehyde's methyl torsion is at 143.3 cm^{-1} [13]). The 230-cm^{-1} fundamental is therefore the skeletal torsion. This fundamental interacts with a ground-state fundamental at 101 cm^{-1} which has previously been assigned to the skeletal torsion by Fateley and coworkers.[8]

The weak nontotally symmetrical fundamental at 607 cm^{-1} is tentatively assigned to the vinyl CH_2 out-of-plane deformation. The intensity and frequency shift are similar to those found in both acrolein and methacrolein.

The strong band at 1460 cm^{-1} is assigned to the excited-state asymmetric methyl bending. The intensity of this fundamental is remarkable and supports the assignment of the strong combination band at 35 cm^{-1} as resulting from ground- and excited-state methyl torsion interaction. Apparently, the close proximity of the methyl group to the oxygen atom, which is the origin of the $n \rightarrow \pi^*$ transition vector, produces a large degree of vibronic activity.

The strong system origin, the apparent lack of out-of-plane bending modes, and the increase in the electron density of the central C–C bond indicate that the first excited singlet state is planar or very nearly planar. The fractional intensity of the system origin is ~0.20, but the approximate nature of this calculation does not warrant comparison with the more accurate values obtained for the other compounds. The change on excitation for the skeletal torsion, ∠CCO in-plane bending, and carbonyl and C=C stretching is larger for this molecule than for any of the aldehydes and indicates that methyl vinyl ketone experiences the greatest excited-state geometry change.

(B) Ground-State Vibrational Assignments. A partial list of tentative ground-state vibrational assignments for the four molecules investigated in this report is given in Table V. Only those types of vibrations which were found to have potential vibronic activity have been assigned. These fundamentals include the carbonyl and C=C stretching vibrations, the symmetric and asymmetric methyl bending modes, the in-plane and out-of-plane hydrogen deformations, and triatomic bending vibrations, and the methyl, C=C, and skeletal torsions.

The structural similarities in these molecules, the fact that acrolein has been previously assigned,[2] and the extensive literature on compounds of similar structure[14] made it possible to analyze the ground-state fundamentals with a degree of confidence. One should recognize, however, that the large number of fundamentals associated with these molecules (27 for the singly substituted methyl derivatives), and the fact that few symmetry restrictions interfere with the interaction of these fundamentals with one another, produces a highly complicated spectrum in which very few vibrations can be treated as "pure," *i.e.*, associated with a single, unperturbed group frequency. Therefore, all of the assignments should be considered as "approximate descriptions."

All of the molecules investigated here are planar (except for the methyl group) and belong to the C_s point group. Consequently, it is only possible to classify the vibrations as either *totally symmetrical* with respect to the molecular plane (*i.e.*, in-plane vibrations) or *nontotally symmetrical* with respect to the molecular plane (*i.e.*, out-of-plane vibrations). The band shapes

---

(12) P. D. Foster, V. M. Rao, and R. F. Curl, Jr., *J. Chem. Phys.*, **43**, 1064 (1965).

(13) F. Winther and D. O. Hummel, *Spectrochim. Acta, Part A*, **25**, 417 (1969).

(14) L. J. Bellamy, "The Infrared Spectra of Complex Organic Molecules," 2nd ed, Wiley, New York, N. Y., 1958, and references therein.

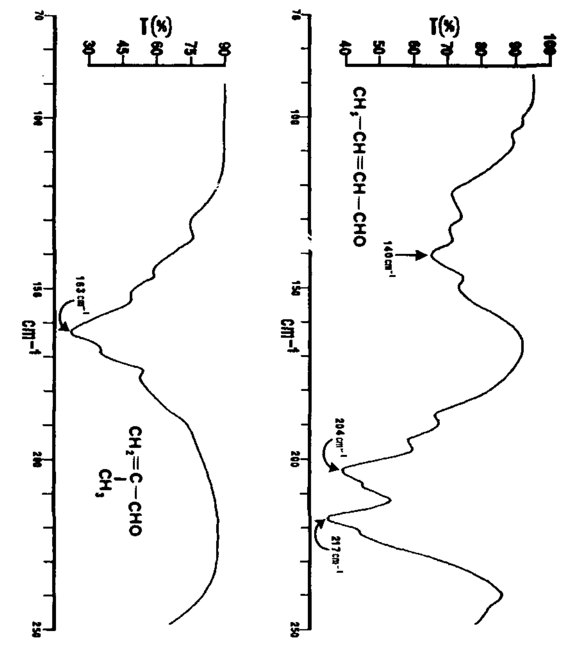

Figure 7. Far-infrared spectra of crotonaldehyde (top) and methacrolein.

(polarities) of the vapor-phase vibrations are designated using the following convention. Type α bands exhibit submerged or partially submerged Q branches and well-developed P and R branches. Type β band shapes exhibit P, Q, and R branches of roughly equal intensity. The two preceding classifications are associated with vibrations whose dipole moment remains within the plane of the molecule. Type γ band shapes exhibit a strong Q branch and a very weak or nonexistent P and R structure and are associated with out-of-plane vibrations. The present convention purposely avoids the more precise type A, B, or C symmetry classifications since the low symmetry of the molecules prevents differentiation between type A and type B vibrations. All of the in-plane vibrations appear to be hybrids of A and B, most of which exhibit a slight predominance of A type symmetry. Each molecule will be briefly discussed, emphasizing those assignments which are unusual.

All 18 ground-state fundamentals of acrolein have been assigned by Brand and Williamson through observation of the vibrational isotopic shifts between the normal and $CH_2{=}CHCDO$ isomers.[2]

Crotonaldehyde was investigated in the vapor phase from 2000 to 20 cm^{-1} and in solution (CCl_4) from 2000 to 400 cm^{-1}. An interesting abnormality in the spectrum involves the methyl bending modes. Normally, the symmetric bending of the methyl hydrogens has a greater infrared absorption intensity than the asymmetric methyl (strictly speaking, nonsymmetric) bending. Not only is the asymmetric methyl bending stronger in crotonaldehyde, but this bending mode appears to split into two nondegenerate fundamentals involving a medium intensity band at 1447 cm^{-1} and a medium-to-weak band at 1460 cm^{-1}. Judging from the band shapes of the two vibrations, the higher frequency fundamental is associated with the symmetrical component (with respect to the molecular plane) of the nonsymmetrical (with respect to the local symmetry of the methyl group) methyl bending. The low-frequency fundamental is associated with the antisymmetrical component.

Table V. Ground-State Fundamentals of the Singly Substituted Methylpropenals

		$CH_2{=}CHCHO$[a]				$CH_3CH{=}CHCHO$				$CH_2{=}C(CH_3)CHO$				$CH_2{=}CHCOCH_3$			
Assignment	Mode	Vapor	Liquid	Pol[f]	Intensity	Vapor	Liquid	Pol[f]	Intensity	Vapor	Liquid	Pol[f]	Intensity	Vapor	Liquid	Pol[f]	Intensity
C=O stretch (s-trans)	a′	1723	1704	α	1000	1720	1699	α	1000	1717	1703	α	1000	1724	1705 }	d	1000
C=O stretch (s-cis)	a′													1703	1685 }		
C=C stretch	a′	1625	1620	β	61	1644	1644	β	230	1645	1637	β	110	1630	1617	β	140
CH_3 asym bending	a′, a″					1447	1445	βγ	170	1455	1450	βγ	185	1430	1425	Sh	350
CH_3 sym bending	a′					1391	1393	β	50	1375	1380	βγ	240	1370	1361	β	500
Vinyl CH_2 in-plane deform	a′	1422	1419	β	56					1425	1423	β	160	1400	1398	β	550
Vinyl CH in-plane deform	a′	1276	1274	α	8	1305	1304	α	30					1250	1246	α	450
Formyl CH in-plane deform	a′	1361	1361	β	19	1377	1377	β	50	1365	1363	β	250				
Vinyl CH_2 out-of-plane deform	a″	959	963	γ	224					957	962	γ	275	953	955	γ	670
Vinyl C=C torsion[b]	a″	993	986	γ	117	974	971	γ	380					988	983	γ	250
Formyl CH out-of-plane deform	a″	980	Hidden	?	?	935	932	γ	320	932	939	γ	690				
∠CCO in-plane bending	a′	564	565	β	31	537	544	α	110	630	?	β	120	490	485	β	140
In-plane bending	a′	340	330	α	32	280	?	βα	90	268	?	β	110	283	?	α	230
Out-of-plane bending	a″					730	?	βγ	50	814	?	βγ	125	598	599	βγ	140
Out-of-plane bending	a″					455	462	βγ	30	420	?	βγ	135				
Skeletal torsion	a″	158[e]	182[c]	γ	?	206[e]	?	γ	2×	163	?	γ	?	101[c]	?	γ	?
Methyl torsion	a″					140	?	γ	1×	?	?	?	?	111[e]	?	γ	?

[a] Vapor-phase data from ref 2. [b] More commonly described as the vinyl CH wag or out-of-plane deformation. [c] From ref 8. [d] See discussion in section II.B of text. [e] From the electronic spectrum. [f] Polarity.

Table VI.

Combination band, cm^{-1}	Calcd torsional value, cm^{-1} Skeletal	Methyl
−409		111.2
−354	101.8	
−243	100.4	
−174	101.0	
−75		111.0
−41		111.7
35		112.0
106		111.7
	Av 101.1 ± 0.7	111.5 ± 0.5
	Obsd (101)[a]	(111)[b]

[a] Far-infrared spectrum (ref 8 and 15). [b] Electronic spectrum (see Table IV).

Table VII. Comparison of Ground-State (S_0) and First-Excited-Singlet-State ($S_1(n,\pi^*)$) Fundamentals of the Singly Substituted Methylpropenals

	$CH_2{=}CHCHO$			$CH_3CH{=}CHCHO$			$CH_2{=}C(CH_3)CHO$			$CH_2{=}CHCOCH_3$		
Assignment	Ground	Excited	Intensity[a]	Ground	Excited	Intensity	Ground	Excited	Intensity	Ground	Excited	Intensity
C=O stretch	1723	1266	11	1720	1238	5	1717	1222	7	1724	1191	m
C=C stretch	1625	1410	13	1644	1363	8	1645	1320	13	1630	1305	s
CH_3 asym bending				1447	1455	4	1455	1457	3	1430	1460	ss
CH_3 sym bending				1391			1375	1356	12	1370		
Vinyl CH in-plane deform	1276			1305	1019	3				1250	940	w
Formyl CH in-plane deform	1361	1133	3	1377	1142	4	1365	1104	5			
Vinyl CH_2 out-of-plane deform	959	582	<1				957	567	2	953	607	w
Formyl CH out-of-plane deform	980	644	<1	935	673	3	932					
∠CCO in-plane bending	564	488	7	537	457	5	630	535	5	490	381	s
Vinyl C=C torsion	993	333	2	974	375	3	?	394	3	988		
Skeletal torsion	158	250	1	206	243	3	163	233	1	101	230	mw
Methyl torsion				140	187	4	?	183	1	111	147	mw

[a] Relative intensity of first quantum transition (system origin = 10).

The far-infrared spectrum of crotonaldehyde provides evidence for three low-frequency, nontotally symmetrical fundamentals at 140, 204, and 217 cm^{-1} (Figure 7). The lowest frequency band is assigned to the methyl torsion on the basis of its intensity and its interaction with the excited-state methyl torsion (section II.A.2). The fundamental at 204 cm^{-1} (206 cm^{-1} from the electronic spectrum) is assigned as the skeletal torsion because of its interaction with the excited-state skeletal torsion (section II.A.2). The remaining fundamental at 217 cm^{-1} is probably associated with a ∠CCC out-of-plane bending.

Methacrolein was investigated in the vapor phase from 2000 to 20 cm^{-1} and in solution (CCl_4) from 2000 to 900 cm^{-1}. Our assignments below 850 cm^{-1} agree with those of Harris and Witkowski (H–W),[15] with the additional assignment of the band at 630 cm^{-1} (H–W, 628 cm^{-1}) to the in-plane bending of the CCO moiety. The far-infrared spectrum is shown in Figure 7. The strong peak at 163 cm^{-1} (H–W, 165 cm^{-1}), which strongly interacts with the excited-state skeletal torsion, is assigned to the ground-state skeletal torsion. The methyl torsion does not appear to be of sufficient intensity to be observed in the ir, although it is possible that it is hidden beneath the broad absorption associated with the skeletal torsion. Calculations based on the intensity of the excited-state methyl torsion and the possible combinations of this torsion with a ground-state vibration indicate that the methyl torsion is probably in the region of 132 or 264 cm^{-1} (see section II.A.3). Although a band does appear at 268 cm^{-1}, it has a band shape associated with a totally symmetrical vibration and an intensity much greater than is normally associated with methyl torsions. A very weak band also appears in the far-infrared spectrum at about 130 cm^{-1}, but it is probably a hot band associated with the 163-cm^{-1} fundamental. The actual frequency of the ground-state methyl torsion, therefore, remains unresolved.

Methyl vinyl ketone was investigated in the vapor phase from 2000 to 200 cm^{-1} and insolut ion (CCl_4) from 2000 to 400 cm^{-1}. The far-infrared spectrum has been previously investigated[8,14] and is reproduced in ref 8. The energetic differential between the s-trans and s-cis conformations is small enough to allow a significant amount of the mestastable s-cis isomer to be present at room temperature.[9] While the carbonyl stretching fundamentals associated with both of the conformations are resolved in solution, the vapor-phase carbonyl region exhibits a very complicated polyad exhibiting a central maximum at 1714 cm^{-1}. At higher resolution it becomes apparent that the central maximum results from an overlapping of the P branch of the s-trans component with the R branch of the s-cis component. The Q branch of the s-trans component is found at 1723.5 cm^{-1}, while the s-cis absorption is centered around 1703 cm^{-1}.

The ground-state skeletal torsion appears in the far-infrared at 101 ± 2 cm^{-1} (ref 8 and 15). A fundamental associated with the ground-state methyl torsion appears in the hot-band region of the vibrational-electronic spectrum at 111 cm^{-1}. Because of the resolution of our instrument, however, it was conceivable that these two values might be associated with the identical fundamental. The appearance and analysis of the eight torsional combination bands, however, indicate that the 111-cm^{-1} fundamental is indeed a distinct fundamental. More precise values for these two torsions can be derived by calculating the wavenumber of the torsion that best corresponds with the observed separation of the combination band from the system origin. From this analysis, which is presented

---

(15) R. K. Harris and R. E. Witkowski, *Spectrochim. Acta*, 20, 1651 (1964).

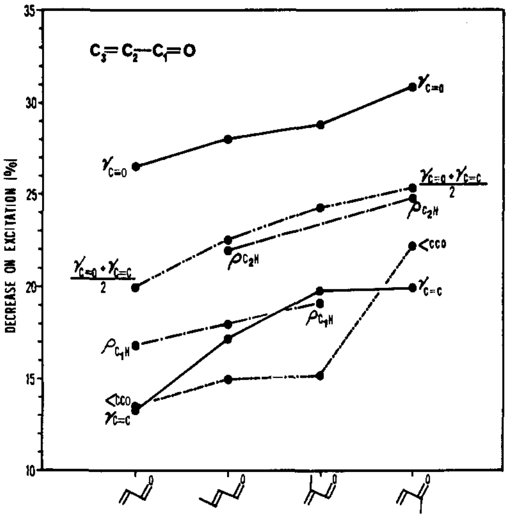

Figure 8. Percentage decrease in vibrational frequency on excitation ($S_0 \rightarrow S_1(n,\pi^*)$) for the totally symmetrical fundamentals of the singly substituted methylpropenals.

in Table VI, the best values for the two torsions are 101.1 and 111.5 cm^{-1} for the skeletal and methyl torsions, respectively.

(C) Comparison of Ground- and Excited-State Fundamentals. A tabulation of the ground-state and first-excited-singlet-state fundamentals of the singly substituted methylpropenals is presented in Table VII. All of the molecules exhibit similar vibrational shifts upon excitation, the most significant being the drop in the carbonyl and C=C stretching frequencies, the decrease in the ∠CCO in-plane bending frequency, and the increase in the frequency of the skeletal torsion. It is interesting to note that all of the in-plane and out-of-plane hydrogen deformations exhibit a drop in frequency, which not only indicates a significant reorganization of the electron density in the mobile π system, but also an overall increase in the free valence indices at all of the carbon atoms. The percentage decrease on excitation for the totally symmetrical fundamentals of all of these compounds appears to change in a smooth manner with position of methyl group substitution. As the methyl group is attached at positions closer to the oxygen atom, the percentage decrease in frequency becomes greater (see Figure 8). This observation has important implications with respect to the mechanism through which the methyl group influences the energy and geometry of the first excited singlet state. A detailed analysis of this interaction is presented in the accompanying paper.[6]

Acknowledgments. We are grateful for the advice and criticism of Professor G. W. Robinson and wish to thank the U. S. Army Research Office (Durham) for partial financial support. We also wish to thank the Connecticut Research Commission for support of special instrumentation.

Excited-State Geometries of the Singly Substituted Methylpropenals.[1a] II. Bond Order Reversal and Substituent Interaction in $S_1(n,\pi^*)$

Robert R. Birge* and Peter A. Leermakers[1b]

Contribution from the Hall-Atwater Laboratories, Wesleyan University, Middletown, Connecticut 06457.

Received March 8, 1971

Abstract: The first excited n,π^* singlet-state geometries of acrolein and its singly substituted methyl derivatives have been analyzed and compared. Excited-state bond length changes were calculated using force constant relationships and compared, where possible, to the more accurate values obtained from Franck-Condon calculations. The relative degree of bond order reversal (RDBOR) is defined and used as a quantitative measure of the degree of excited-state methyl group electron injection into Ψ_3. The methyl group was found to perturb both ground-state n-electron and excited-state Ψ_3 wave function energies *via* similar mechanisms involving "hyperconjugative" reorganization of π-system electron distribution.

Alkyl substitution normally produces a blue shift in the n $\rightarrow$ π^* transition.[2] Sidman has associated the increased energy of the transition with the electron-donating character of alkyl groups and their tendency to accumulate electronic charge in a localized region of the excited-state molecular orbital, thereby increasing its energy.[2] The present report investigates the nature of this substituent-induced blue shift for the singly substituted methylpropenals utilizing the information afforded by the vibrational analysis (discussed in the previous paper[3]) to calculated excited-state bond lengths. These bond lengths are used to define the relative degree of bond order reversal (RDBOR), a quantitative measure of the total relative electron density in the Ψ_3 (Ψ_3 is defined as the lowest antibonding π molecular orbital) molecular orbital. The latter variable assists in defining the degree of substituent (methyl group) electron injection into the singly occupied excited-state MO and allows a quantitative description

---

(1) (a) Abstracted from a portion of the Ph.D. thesis of R. R. B., Wesleyan University, 1971; (b) deceased Aug 16, 1971.

(2) J. Sidman, *Chem. Rev.*, **58** 689 (1958).

(3) R. R. Birge, W. C. Pringle, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **93** 6715 (1971).