Electronic and Vibrational States of Acrolein

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Eastwood and Snow¹⁾ carried out a vibrational and rotational analysis of the near ultraviolet spetrum of acrolein. Walsh²⁾ also studied the electronic spectrum of this compound in the vacuum ultraviolet region. Interest in this compound lies partly in the fact that it has a simple skeletal structure containing a system of conjugated double bonds, and that its electronic states can easily be discussed in terms of the MO theory³⁾. In a previous paper⁴⁾ we studied the n-π^* absorption bands of acrolein as measured with a photoelectric spectrometer. This time the absorption spectrum was measured photographically. In this paper is reported the results of our continued study on the electronic and vibrational states of the molecule. For aiding vibrational analysis, infrared and Raman spectra were also observed, although they have already been measured⁵⁾. Using our new results, more detailed vibrational assignments for the excited state could be made.

Experimental

Acrolein supplied by Tokyo Kasei Kogyo Co. was used. The sample was distilled before measurement. An absorption tube of 40 cm. length provided with quartz windows was used. The spectrum was photographed at various vapor pressures corresponding to temperatures between −25 and 180°C of the tube. The tube with the windows was always kept at temperature about 10°C higher than that of the sample site for purpose of avoiding condensation. A hydrogen or a tungsten lamp was used as the source of the continuum. A Shimadzu type QL-170 spectrograph was used throughout the work. Exposure time from 1 to 20 min. for the tungsten lamp and from 2 to 3 hr. for the hydrogen lamp with a slit width of 20 μ. Fuji process plates were used. Wavelengths were determinined relative to those of iron lines, using a Shimadzu type SR-2 comparator.

For infrared and Raman measurements carbon tetrachloride or ethyl alcohol solution was used. Solvents were purified by Weissberger and Proskauer methods⁶⁾. The Raman spectrograph used was of two dense flint prisms, having the linear dispersion of 24 Å/mm. at 4500 Å. Raman spectrum of acrolein was obtained with ethyl alcohol solution, as acrolein is very unstable chemically under strong irradiation and it was difficult to work with the liquid state. Renewing the sample at about one hour intervals a 12 hr. exposure was made with a slit width of 100 μ. During the exposure filter solution of sodium nitrous oxide was circulated. The infrared absorption was measured with a Hitachi EPI double beam spectrometer with sodium chloride or potassium bromide prism. For acrolein vapor in the sodium chloride region a 10 cm. gas cell was used.

Electronic Transition

Acrolein is a simple aliphatic aldehyde having a system of conjugated double bonds. Electron diffraction study⁷⁾ shows that the molecule has a planar *trans*-butadiene-like structure. The molecule thus belongs to the point group Cs and the electronic transitions are all symmetry-allowed. The molecule has four π-electrons and a pair of nonbonding electrons localized on the oxygen atom. Therefore n-π^* and π-π^* transitions are expected to occur. The absorption spectrum of acrolein solution in carbon tetrachloride in the 24993∼33324 cm⁻¹ region shows a blue shift on addition of ethanol. In ethanol solution the acrolein absorption maximum shifts toward the blue by 400 cm⁻¹ relative to carbon tetrachloride solution⁴⁾. The above result suggests the n-π^* nature of this electronic transition. Walsh attributed this transition to a one-electon promotion from the n orbital to the first excited π orbital. His assignment agrees with our calculation³⁾.

According to the MO theory this first excited state has A′ symmetry, and the lowest state is triplet. Consequently, the vapor absorption begining at 25851 cm⁻¹ is assigned to the transition of a nonbonding electron to the first excited singlet state ($^1A''-{}^1A'$).

Vibrational Analysis

On account of the low Cs symmetry of the molecule, the transition can be of an allowed type. So the 0, 0 band will probably be one

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1) E. Eastwood and C. P. Snow, *Proc. Roy. Soc.*, **149A**, 446 (1935).

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

3) K. Inuzuka, This Bulletin, **34**, 6 (1961).

4) K. Inuzuka, ibid., **33**, 678 (1960).

5) M. Aime Cotton, *Compt. rend.*, **208**, 740 (1939).

6) A. Weissberger and E. S. Proskauer, "Organic Solvents", Interscience Publishers, Inc., New York, N. Y. (1955).

7) H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 691 (1951).

of the stronger bands. The development of the spectrum with increasing temperature suggests that the 0, 0 band is surely the strong band at 25851 cm^{-1}. In an earlier work of Eastwood and Snow a band at 25860 cm^{-1} was chosen as the 0, 0 band from rotational analysis, and two progressions of bands with mean separations of 1260 and 500 cm^{-1} respectively were observed. Since our measurement was limited to about 30294 cm^{-1}, the progression corresponding to 1260 cm^{-1} could not be followed further than the second overtone. These bands are accompanied each by a strong subsidary band with the separation of 499 cm^{-1}. In our analysis 1270 cm^{-1} was taken as the interval of the progression. Among the observed bands, nearly 130 in number, some show rotational structures but many are not well defined. It is difficult to interpret correctly all of these observed bands on account of the low symmetry of the molecule, so we give in Table I the position and interpretations only for stronger bands. The frequencies of 1270 and 499 cm^{-1} are assigned definitely to two totally symmetric vibrations of type A' of the lower electronic state. The very weak bands on the longer wavelength side of the 0, 0 band decrease their intensity with decreasing temperature, and the vicinity of 70°C is favorable for their observation. The number of moderately strong bands is small on this side of the 0, 0 band. A sharp band is separated from the 0, 0 band by 145 cm^{-1}, and three fine bands by about 313 cm^{-1}. The latter bands are the ones called by Eastwood and Snow a, b and c bands, although our wavelengths are slightly different from that of Eastwood and Snow.

Table I. Vibrational analysis of ultraviolet absorption spectrum of acrolein vapor

In.	Å	cm^{-1}	Freq. distance from the 0, 0 band	Assignment
vs	3867.2	25851	0	0, 0
vs	3794.0	26350	499	0+499
m	3705.7	26978	1127	0+1127
vs	3686.2	27121	1270	0+1270
vs	3666.6	27265	1414	0+1414
bm	3638.5	27476	1625	499+1127=1626
s	3620.0	27616	1765	1270+499=1769
bs	3601.6	27758	1907	499+1414=1913
m	3538.3	28254	2403	1270+1127=2397
s	3521.3	28391	2540	2(1270)
bm	3502.2	28545	2694	1270+1414=2684
m	3484.1	28693	2842	2(1414)
m	3461.6	28880	3029	2(1270)+499=3039
w	3387.4	29513	3662	2(1270)+1127=3667
w	3369.0	29674	3823	3(1270)
w	3354.1	29806	3955	2(1270)+1414=3954
w	3324.5	30071	4220	3(1414)

vs : very strong, s : strong, bm : broad medium, m : medium, w : weak

In addition, there is a series of four bands 24636, 24611, 24577 and 24552 cm^{-1} on the further long wavelength side. Among these bands the second one which is separated from the 0, 0 band by 1240 cm^{-1} is the strongest. On the whole our observation agrees well with that of Eastwood and Snow. Besides these bands, two weak but sharp bands are observed at 24259 and 24240 cm^{-1}. There are no further bands on the red side of these two bands. The bands on the red side of the 0, 0 band having appreciable intencities usually represent fundamental vibrational frequencies of the ground state. From this viewpoint we may assign the two bands separated from the 0, 0 band by 1274 and 1611 cm^{-1}, respectively, to the two frequencies 1270 and 1623 cm^{-1} found in infrared and Raman spectra. Bands other than those described above are tentatively interpreted as combination bands. A band with moderate intensity separated by 1127 cm^{-1} from the 0, 0 band on its shorter wavelength side form a satellite accompanying the stronger 1270 cm^{-1} band. The 1127 cm^{-1} frequency appears also in other combination bands, so that it is reasonable to assume this frequency as a fundamental. There is a very strong band at 27265 cm^{-1} separated by 1414 cm^{-1} from the 0, 0 band. Starting from this band a progression containing two more bands with 1414 cm^{-1} interval is observed. The 1414 cm^{-1} frequency also appears in other combination bands, so that we may assume this to be another fundamental.

Fundamental Vibrational Frequencies

The acrolein molecule, CH_2CHCHO, may belong, at the most, to the point group Cs. As it contains eight atoms, eighteen normal modes of vibration are possible, of which thirteen are of the totally symmetrical A' type, and the remaining five are of the anti-symmetrical A'' type. Both types are active in infrared and Raman spectra. There will be seven essentially valency type vibrations of the four C–H, one C=C, one C–C and one C=O bonds. Analogously to 1, 3-butadiene[8,9] there will also be an A'' type torsional oscillation about the C–C bond. Another important mode of A' is the planar deformation of the C=C–C=O skeleton.

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[8] C. M. Richards and J. R. Nielsen, *J. Opt. Soc., Am.* **40**, 438 (1950).

[9] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 131 (1947).

TABLE II. INFRARED AND RAMAN FREQUENCIES OF ACROLEIN MOLECULE (cm^{-1})

Infrared				Raman EtOH solution		Assignment
CCl_4 solution		vapor				
w	570			w m	340 574	Skeletal bending Skeletal bending
s s s	910 959 982	m s s s	906 917 960 990	w	980	CH and CH_2 wagging
s	1152	s	1147 1156 1163	w	1170	CH_2 rocking
w	1270	w	1262 1280	m	1272	C–C stretching
m	1360	m	1348 1366	s	1360	CH rocking
m	1420	m	1410 1427	w	1426	CH_2 deformation
m	1617	m	1613 1632	s	1620	C=C stretching
vs	1708	vs	1713 1727	vs	1701	C=O stretching
m m m w w	2700 2755 2805 2990 3100	m m m w w	2710 2790 2810 3000 3100			C–H stretching
w	3375	w	3388			C=O overtone

The infrared spectrum was measured in the 460∼4000 cm^{-1} region, but a weak band at 340 cm^{-1} was found in the Raman spectrum. An analogous band was found in 1, 3-butadiene at 320 cm^{-1} and has been assigned to a skeletal deformation vibration. Therefore we have assigned the Raman band of acrolein at 340 cm^{-1} to an A'' type skeletal deformation vibration. We found a weak band at 570 cm^{-1} in the infrared potassium bromide region, and in the Raman spectrum at 574 cm^{-1}. It may be assigned to an A' type skeletal deformation vibration. In 1, 3-butadiene the corresponding Raman band is at 513 cm^{-1}. Corresponding to the infrared bands in the 900 cm^{-1} region only one Raman band at 980 cm^{-1} was found with very small intensity. This band system may be due to the CH and CH_2 wagging vibrations. The infrared band at 1150 cm^{-1} is strong and sharp, and the corresponding Raman band has exactly the same frequency shift.

This band may be assigned to the rocking vibration of the methylene radical. The Raman band at 1272 cm^{-1} has medium intensity. In infrared two bands appear at 1235 and 1270 cm^{-1}, the former being very weak, and the latter medium strong. We may assign the latter frequency 1270 cm^{-1} to the C–C stretching vibration, in analogy to the 1205 cm^{-1} of 1, 3-butadiene and 1284 cm^{-1} of biacetyl[10]. The value of 1270 cm^{-1} for acrolein might appear too high for the C–C stretching frequency, but it is probably due to the partial double bond character of the bond in this molecule, whose length is 1.46 Å[7], considerably shorter than the normal C–C single bond length 1.53∼1.54 Å. The band at 1360 cm^{-1} was observed in both the Raman and infrared spectra with considerable intensity. This frequency may be assigned to the CH rocking vibration. The weak band at 1420 cm^{-1} in infrared and at 1426 cm^{-1} in Raman spectra may be assigned to the CH_2 deformation vibration in analogy to the Raman 1442 cm^{-1} band in 1, 3-butadiene. The C=C stretching frequency is observed as the 1617 cm^{-1} infrared band for solution, as the 1620 cm^{-1} Raman medium strong band. The C=O stretching frequency is observed at 1695∼1725 cm^{-1} in solution with two peaks in the infrared and at 1700 cm^{-1} in the Raman spectrum. It is the strongest band in both the spectra, but the Raman frequency seems to have been affected by the solvent. C–H valence vibration bands lying in the 2700∼3000 cm^{-1} region were not observed in the Raman spectrum as they may be hidden under excited Hg lines. Result of the vibrational analysis is given in Table II.

In a symmetry-allowed molecular electronic

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[10] J. W. Sidman and D. S. McClure, *J. Am. Chem. Soc.*, 77, 6471 (1955).

TABLE II. FUNDAMENTAL VIBRATIONAL FREQUENCIES (cm^{-1})

Raman (solution)	Infrared (vapor)	Lower state	Upper state	Assignment
1701	1713 1727	1720	1270	C=O valence (A′)
1620	1613 1632	1623	1414	C=C valence (A′)
1272	1259 1280	1270	1127	C–C valence (A′)
570		570	499	C=C–C=O bending (A′)

transition, totally symmetric vibrational frequencies appear generally with large intensities in absorption. In the acrolein spectrum as analyzed above, all of the interval frequencies contained in prominent progressions can be assigned either to fundamental, or to combination frequencies of A′ type vibrational modes of the excited electonic state. In Table III correlations among upper and lower state vibrational frequencies are given. Of these fundamental frequencies those of the upper state of 1270 cm^{-1} and 499 cm^{-1} are the most important in the vapor absorption. The former is observed up to the second overtone (3×1270 cm^{-1}) and is assigned to the C=O stretching mode. The latter frequency is assigned to a skeletal bending mode, as its corresponding lower state frequency is very probably 570 cm^{-1} observed in both Raman and infrared spectra. The very strong band separated from the 0, 0 band by 1414 cm^{-1} may be associated with another fundamental vibration, since we could not analyze so strong a band as a combination or overtone and since, moreover, its frequency separation 1414 cm^{-1} is repeated twice more in forming a prominent progression. In our previous paper(4) this frequency was assigned to the C=C vibration, although a slightly different value was then reported. The 1127 cm^{-1} frequency is observed as satellite bands accompanying each of the 1270 cm^{-1} progression bands. This frequency was not reported in the above cited paper(4). It can be assigned to the C–C vibration of the excited electronic state in analogy to the biacetyl 1136 cm^{-1} (excited state) and 1284 cm^{-1} (ground state). In acrolein the corresponding lower state frequency is 1270 cm^{-1}.

Summary

The position, blue-shift and theoretical calculation(3) of the state energy of the electronic transition of acrolein in 24241~30294 cm^{-1} region suggest that the transition is of the $n-\pi^*$ type. From the vibrational analysis of acrolein vapor spectrum, it is known that the vapor spectum of acrolein has four progressions corresponding to the C=O, C=C and C–C stretching, and skeletal bending frequency in the lower state.

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