Force Constants and Mean Amplitudes of Acrolein

Tsutomu FUKUYAMA, Kozo KUCHITSU and Yonezo MORINO

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received May 22, 1968)

As mentioned in the preceding note for glyoxal,[1] the force constants were estimated for acrolein in order to obtain the correction terms necessary for correlating the structural data observed by electron diffraction and spectroscopy.

Observed Vibrational Frequencies. Acrolein is a planar molecule (C_s symmetry) with eighteen fundamental frequencies: 13A′+5A″. All but one of them were assigned by Brand and Williamson[2] on the basis of the observation of near-ultraviolet spectra. They assigned most of the fundamental frequencies of CH_2=CHCDO as well. On the other hand, Harris observed infrared and Raman spectra and assigned the fundamentals of the normal species.[3] His assignment differs from that of Brand in that the schematic descriptions of the 1158 cm^{-1} (ν_{10}) and 912 cm^{-1} (ν_{11}) modes are interchanged. We accepted the assignment of Harris since it is consistent with a

TABLE 1. UREY-BRADLEY FORCE CONSTANTS FOR ACROLEIN[a] (in mdyn/Å)

	K		H	F
C-H$_1$	4.64	H$_1$C$_2$H$_3$	0.262	0.21
C-H$_4$	4.46	H$_1$C$_2$C$_5$	0.190	0.52
C-H$_7$	3.78	C$_2$C$_5$C$_6$	0.325	0.35
C=C	7.14	C$_2$C$_5$H$_4$	0.186	0.52
C-C	3.46	H$_4$C$_5$C$_6$	0.259	0.27
C=O	10.30	H$_7$C$_6$O$_8$	0.375	0.61
		C$_5$C$_6$O$_8$	0.500	0.46
		H$_7$C$_6$C$_5$	0.200	0.20

p(CH, CH)	f(CC, CO)	f(CCC, CCO)
−0.157	−0.681	0.209

a) Numbering of atoms:

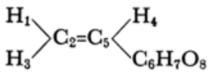

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES OF ACROLEIN (in cm^{-1})

			CH_2=CHCHO		CH_2=CHCDO	
			Obsd	Calcd	Obsd	Calcd
A′	ν_1	CH_2 str	3103	3103	3101	3103
	ν_2	CH_2 str	3000	3009	2988	3009
	ν_3	CH str	3000	2991	—	2991
	ν_4	formyl CH str	2800	2801	2060	2098
	ν_5	C=O str	1724	1728	1709	1695
	ν_6	C=C str	1625	1619	1621	1618
	ν_7	CH_2 scis	1420	1413	1403	1413
	ν_8	HCO bend	1360	1360	—	1033
	ν_9	CH bend	1275	1270	1275	1275
	ν_{10}	C-C str	1158	1147	1153[a]	1169
	ν_{11}	CH_2 rock	912	915	877[a]	871
	ν_{12}	C-C=O bend	564	566	562	563
	ν_{13}	C-C=C bend	327	324	—	313
A″	ν_{14}	CH_2 twist	993	1002	993	997
	ν_{15}	formyl CH wag	980[b]	990	846	866
	ν_{16}	CH_2 wag	959	955	959	962
	ν_{17}	CH wag	593	592	556	557
	ν_{18}	torsion	157	157	151	149

a) The assignments are interchanged in the original report by Brand.[2] See text.
b) Evaluated by the product rule.

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[1] T. Fukuyama, K. Kuchitsu and Y. Morino, This Bulletin, **42**, 3019 (1968).

[2] J. C. D. Brand and D. G. Williamson, *Discussions Faraday Soc.*, **35**, 184 (1963).

[3] R. K. Harris, *Spectrochim. Acta*, **20**, 1129 (1964).

recent assignment of the fundamentals of butadiene reported by Abe and Shimanouchi.[4]

In-plane Vibrations. The potential energy was expressed in terms of *K, H, F* and three additional force constants. One interaction constant was introduced between the two C–H stretching coordinates of the methylene group. The other constants were introduced between the C=C and the C=O stretching coordinates and between the CCC and the CCO bending coordinates. Initial values of the force constants were taken from those for butadiene and glyoxal. After several trials, they were adjusted by a least-squares method with K_{C-C}, H_{HCH} and f(CCC, CCO) as variable parameters. The result is shown in Table 1, and the calculated frequencies are compared with observed values in Table 2.

The force constants for the vinyl group, including p(CH, CH), are close to the corresponding constants for butadiene, except for the C=C stretching force constant $K_{C=C}$ (7.1 mdyn/Å), which is larger than that for butadiene (6.6 mdyn/Å).[4] The force constants for the aldehyde group are roughly equal to those for glyoxal. A systematic decrease in the C–C stretching force constant observed for butadiene (3.82 mdyn/Å), acrolein (3.46 mdyn/Å) and glyoxal (3.25 mdyn/Å) correspond to a systematic increase in the bond distance r_g(C–C) (1.465, 1.480, and 1.526 Å, respectively)[5] and a systematic decrease in the π-bond order (0.224, 0.200, and 0.132).

Out-of-plane Vibrations. Abe and Shimanouchi introduced an F_σ matrix of nearly general form in the analysis of the out-of-plane vibrations of butadiene.[4] For acrolein the F_R matrix, which is here equivalent to F_σ, was set up in an analogous manner. Initial values of the elements were transferred from butadiene and glyoxal and then adjusted by trial and error. The final matrix is shown in Table 3. In order to facilitate comparison, notations for the elements are taken from Table 10 of Ref. 4. Effective two-fold torsional barriers around the central C–C bonds are found to be 8.1, 6.3 and 3.7 kcal/mol, respectively, for butadiene, acrolein and glyoxal. They are in essential agreement with the pure torsional transitions observed by Fateley *et al.* in the far infrared;[6] according to their one-dimensional analysis, V_1 and V_3 being ignored, their V_2 values are 7.0, 5.3 and 3.4 kcal/mol, respectively. It is interesting to note that a roughly linear relation exists between the torsional barriers and the lengths of the C–C bonds.

TABLE 3. F_R MATRIX FOR OUT-OF-PLANE VIBRATIONS OF ACROLEIN (in mdyn Å)

$$\begin{array}{l} \text{CH}_2 \text{ wag} \\ \text{CH wag} \\ \text{CH}_2 \text{ twist} \\ \text{C–C torsion} \\ \text{CH formyl wag} \end{array} \begin{bmatrix} F_j & & & & \\ F_{jk} & F_k & & & \\ 0 & F_{kl} & F_l & & \\ 0 & 0 & 0 & F_m & \\ f_{jk} & f_{kk} & f_k & F_k' & \end{bmatrix}$$

F_j	0.327	F_{jk}	−0.054	f_{jk}	0.023
F_k	0.380	F_k	0.034	f_{kk}	−0.018
F_l	0.512	F_k'	0.524	f_{kl}	−0.047
F_m	0.0877				

TABLE 4. MEAN AMPLITUDES FOR ACROLEIN[a] (in Å)

	Calcd	Obsd[b]
C–C	0.0486	$0.042_2 \pm 0.003_2$
C=C	0.0414	$0.047_7 \pm 0.003_3$
C=O	0.0396	$0.036_0 \pm 0.004_5$
C–H_1	0.0774	0.070 ± 0.006
C_2–C_6	0.0704	0.075 ± 0.09
C_2–O_8	0.0653	0.065 ± 0.06
C_5–O_8	0.0579	$0.049_4 \pm 0.003_7$

a) For the numbering of atoms, see footnote of Table 1.

b) Ref. 5.

Mean Amplitudes. Mean square amplitudes for some of the atom pairs of acrolein are calculated from the force constants and compared with the observed values in Table 4. The agreement is as good as that for glyoxal.

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[4] K. Abe and T. Shimanouchi, to be published.

[5] K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Structure,* **1**, 463 (1968).

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