Force Constants and Mean Amplitudes of Glyoxal

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)

In a recent investigation of the gas-phase structures of butadiene, acrolein and glyoxal,[1] a least-squares analysis was carried out on the electron diffraction intensities and rotational constants as joint observables. The method is based on the conversion of electron-diffraction r_a distances into $r_\alpha{}^0$ distances, and that of ground-state rotational constants into average rotational constants. For the conversions, one must know the quadratic force field. The force constants for butadiene were determined by Abe and Shimanouchi,[2] but no data were available on the force fields for glyoxal and acrolein except for the out-of-plane force constants for glyoxal reported by Brand.[3] Thus, a set of force constants have been estimated for the latter molecules from the reported vibrational frequencies of normal and certain deuterated species, at least with sufficient accuracy for calculating small correction terms ($r_\alpha{}^0 - r_a$, $A_z - A_0$, *etc.*).

Observed Vibrational Frequencies. Glyoxal is a molecule with C_{2h} symmetry and has twelve fundamental frequencies: $5A_g + 4B_u + 2A_u + B_g$. In accordance with the rule of mutual exclusion, the B_u and A_u species are infrared active and the A_g and B_g species Raman active. Because of the experimental difficulty, the Raman spectra of glyoxal have never been observed successfully. Harris assigned all infrared-active fundamentals and some combination frequencies, from which he estimated the frequencies of the Raman active fundamentals.[4] The present note on the force constants for glyoxal is mainly based on the frequencies reported by him. The fundamental frequencies of $C_2D_2O_2$ reported by Brand and Minkoff[5] were also taken into account, in addition to the frequencies of the normal species by Harris.

In-plane Vibrations. A modified Urey-Bradley force field was assumed for the description of the in-plane vibrations: The potential

TABLE 1. UREY-BRADLEY FORCE CONSTANTS FOR GLYOXAL (in mdyn/Å)

	K		*H*	*F*		*f*
C-H	3.90	HCC	0.200	0.200	CO, CO	−0.890
C-C	3.25	CCO	0.375	0.410	CCO, CCO	0.225
C=O	10.60	HCO	0.357	0.610		

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

			$C_2H_2O_2$		$C_2D_2O_2$	
			Obsd	Calcd	Obsd	Calcd
A_g	ν_1	C-H str	2844	2840	—	2132
	ν_2	C=O str	1745	1761	1722	1709
	ν_3	C-H bend	1338	1341	—	1129
	ν_4	C-C str	1060	1063	—	915
	ν_5	C-C=O bend	550	542	537	531
B_u	ν_9	C-H str	2836	2840	2141	2116
	ν_{10}	C=O str	1730	1732	1712	1713
	ν_{11}	C-H bend	1312	1310	1008	1006
	ν_{12}	C-C=O bend	341	346	—	320
A_u	ν_6	C-H wag	802	802	630[a]	630
	ν_7	C-C torsion	128	128	117	117
B_g	ν_8	C-H wag	1048	1048	911	911

a) Evaluated by the product rule.

---

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

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

[3] J. C. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954).

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

[5] J. C. D. Brand and G. J. Minkoff, *J. Chem. Soc.*, **1954**, 2970.

energy was expressed in terms of the three sets of force constants (force constants for the bond stretching K, for the valence angle deformation H and for the non-bonded interaction F) and two interaction constants f. The latter constants were introduced between the two coordinates corresponding to the C=O stretching and between the two C–C=O bending coordinates. An apparent difference between the bond-stretching force constant for C–H and that for C–D was taken into account through the relation $K_{\mathrm{C-D}}/K_{\mathrm{C-H}}=1.026$.6)

The force constants transferred from formaldehyde, acetaldehyde and acetone7) were used as initial values, and then adjusted by trial-and-error calculations. In the final stage, a least-squares fit was made by taking $K_{\mathrm{C-C}}$, H_{HCO}, H_{CCO}, f(CO, CO), and f(CCO, CCO) as variable parameters. The result is shown in Table 1 and the frequencies calculated using those force constants are compared with the observed values in Table 2.

The two interaction constants f(CO, CO) and f(CCO, CCO) were essential for reproducing the symmetric and antisymmetric frequencies of the C=O stretching and the CCO bending vibrations. The situation is essentially the same as that for butadiene, as indicated in Table 11 of Ref. 2, where the corresponding force constants, f_{dd} and f_{gg}, are relatively large negative and positive elements, respectively.

Out-of-plane Vibrations. Glyoxal has three out-of-plane vibrations: two in the $\mathrm{A_u}$ species and one in the $\mathrm{B_g}$ species. The number of elements in the F_s matrix are therefore three and one for respective symmetry blocks. The use of the frequencies of $C_2H_2O_2$ and $C_2D_2O_2$ made it possible to determine the F_s matrices uniquely. The result is shown in Table 3 in an internal coordinate system (F_R matrix). Brand determined the out-of-plane force constants by assuming that $(GF)_{76}$ was zero.3) The F_R elements for each isotopic species (also given in Table 3) calculated by his method with the molecular geometry determined recently1) are close to the present estimates.

TABLE 3. F_R MATRIX FOR OUT-OF-PLANE VIBRATIONS OF GLYOXAL[a] (in mdyn Å)

$$\begin{array}{l}\text{CH wag}\\ \text{C-C torsion}\\ \text{CH wag}\end{array}\begin{bmatrix} F_k & & \\ f & F_m & \\ f_{kk} & f & F_k \end{bmatrix}$$

	Present work	Brand[b] Normal species	Brand[b] Deuterated species
F_k	0.480	0.507	0.497
F_m	0.0515	0.0478	0.0491
f_{kk}	−0.049	−0.022	−0.033
f	0.0048	−0.022	−0.017

a) See Ref. 2 for notations.
b) Ref. 3.

TABLE 4. MEAN AMPLITUDES FOR GLYOXAL (in Å)

	Calcd	Obsd[a]
C−C	0.0485	$0.054_6 \pm 0.004_1$
C=O	0.0380	$0.037_1 \pm 0.003_0$
C−H	0.0799	0.057 ± 0.010
C···O	0.0635	$0.059_9 \pm 0.003_7$
O···O	0.0589	$0.060_2 \pm 0.004_0$

a) Ref. 1.

Mean Amplitudes. Mean square amplitudes for several atom pairs of glyoxal were calculated from the derived force constants. The results shown in Table 4 account for the observed values reasonably except for the C–H amplitudes. The small discrepancy in the C–H amplitude may be ascribed to a systematic error included in the diffraction experiment.

The authors are indebted to Mr. Koichi Abe for his helpful information and discussion.

---

6) T. Shimanouchi and I. Suzuki, *J. Chem. Phys.*, **42**, 296 (1965).

7) P. Cossee and J. H. Schachtschneider, *ibid.*, **44**, 97 (1966).