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Mean Amplitudes of Vibration and Related Quantities for Halo Propiolaldehydes and Propiolic Acid Chloride

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The following molecular constants were calculated from spectroscopic data for the halopropiolaldehydes CHOCCCl, CHOCCBr and CHOCCI, and for propiolic acid chloride (CClOCCH): (i) mean amplitudes of vibration, (ii) perpendicular amplitude correction coefficients, and (iii) Bastiansen-Morino linear shrinkage effects. The mean amplitudes were compared with the corresponding values for propiolaldehyde, and characteristic values for some distance types are listed.

Three halopropiolaldehydes have recently been studied spectroscopically.[1] The harmonic force fields previously developed were used to calculate the mean amplitudes of vibration [2] and related quantities, which are reported here. These data are of great interest in gas electron diffraction studies of molecular structures. Similar calculations were also performed for the propiolic acid chloride molecule. They are based on a vibrational assignment of experimental frequencies for this molecule from an original investigation.

HALOPROPIOLALDEHYDES

The halopropiolaldehydes (halopropynals) CHOCCCl, CHOCCBr and CHOCCI have been investigated recently by infrared and Raman spectroscopy.[1] That work includes normal coordinate analyses for the molecules in question, and the main stretching and bending force constants from the developed harmonic force fields are reported. The corresponding vibrational frequencies are shown in Table 1. The force fields were used to calculate the mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K),[2] which are given in Tables 2, 3, and 4 for the chloro-, bromo-, and iodo compound, respectively. The interatomic separations (R) are included in these tables. They give implicit information on the structural parameters applied in the analysis. The Bastiansen-Morino shrinkage effects (δ) for the linear chains in the three halopropiolaldehydes may be obtained very simply from the K values.[2] Their magnitudes are listed in Table 5.

Table 1. Vibrational frequencies (cm^{-1}) for chloro-, bromo-, and iodopropiolaldehyde and for propiolic acid chloride.

Species	CHOCCCl	CHOCCBr	CHOCCI	CClOCCH
a′	2860	2858	2850	3326
	2220	2196	2159	2132
	1694	1692	1676	1767
	1387	1386	1385	1003
	1077	1030	1005	696
	738	691	670	655
	473	395	360	482
	312	290	276	414
	114	105	107	157
a″	945	950	960	703
	352	340	330	665
	152	143	131	224

PROPIOLIC ACID CHLORIDE (PROPIOLYL CHLORIDE)

A normal coordinate analysis was performed for the CClOCCH molecule on the basis of the vibrational assignment of experimental frequencies shown in Table 1. These values are gas infrared frequencies, which have not been published previously. A detailed report on the experimental work is to be communicated later. The developed harmonic force field was used to calculate the u and K values with the results given in Table 6. The linear shrinkage effects are shown in Table 7.

Table 2. Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) for chloropropiolaldehyde, CHOCCCl.

Distance	(R, Å)	u, Å		K, Å	
		$T=0$	298 K	$T=0$	298 K
C_1-H	(1.080)	0.080	0.081	0.019	0.027
$C_1=O$	(1.210)	0.041	0.042	0.003	0.007
C_1-C_2	(1.460)	0.049	0.051	0.005	0.011
$C_2\equiv C_3$	(1.204)	0.036	0.037	0.006	0.009
C_3-Cl	(1.628)	0.038	0.039	0.006	0.018
$C_1\cdots C_3$	(2.664)	0.052	0.055	0.004	0.010
$C_2\cdots Cl$	(2.832)	0.043	0.044	0.002	0.006
$C_1\cdots Cl$	(4.292)	0.054	0.058	0.000_3	0.000_5
$O\cdots H$	(1.984)	0.098	0.100	0.010	0.020
$C_2\cdots H$	(2.208)	0.098	0.100	0.014	0.029
$C_3\cdots H$	(3.338)	0.108	0.111	0.009	0.022
$Cl\cdots H$	(4.922)	0.114	0.130	0.003	0.005
$C_2\cdots O$	(2.316)	0.059	0.066	0.003	0.009
$C_3\cdots O$	(3.433)	0.066	0.082	0.003	0.008
$Cl\cdots O$	(5.008)	0.071	0.108	0.000_1	0.000_2

Table 3. Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) for bromopropiolaldehyde, CHOCCBr.

Distance	(R, Å)	u, Å		K, Å	
		$T=0$	298 K	$T=0$	298 K
C_1-H	(1.080)	0.080	0.081	0.020	0.031
$C_1=O$	(1.210)	0.040	0.041	0.003	0.008
C_1-C_2	(1.460)	0.049	0.050	0.005	0.013
$C_2\equiv C_3$	(1.204)	0.036	0.037	0.006	0.010
C_3-Br	(1.793)	0.039	0.042	0.005	0.015
$C_1\cdots C_3$	(2.664)	0.052	0.054	0.004	0.013
$C_2\cdots Br$	(2.997)	0.043	0.046	0.002	0.005
$C_1\cdots Br$	(4.457)	0.052	0.060	0.000_2	0.000_4
$O\cdots H$	(1.984)	0.098	0.099	0.011	0.024
$C_2\cdots H$	(2.208)	0.098	0.099	0.016	0.035
$C_3\cdots H$	(3.338)	0.108	0.112	0.011	0.027
$Br\cdots H$	(5.084)	0.115	0.134	0.004	0.007
$C_2\cdots O$	(2.316)	0.058	0.065	0.004	0.011
$C_3\cdots O$	(3.433)	0.066	0.081	0.003	0.011
$Br\cdots O$	(5.169)	0.069	0.110	0.000_1	0.000_3

Table 4. Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) for iodopropiolaldehyde, CHOCCI.

Distance	(R, Å)	u, Å		K, Å	
		$T=0$	298 K	$T=0$	298 K
C_1-H	(1.080)	0.080	0.080	0.020	0.034
$C_1=O$	(1.210)	0.040	0.041	0.003	0.008
C_1-C_2	(1.460)	0.048	0.050	0.005	0.014
$C_2\equiv C_3$	(1.204)	0.037	0.037	0.006	0.010
C_3-I	(1.991)	0.042	0.047	0.004	0.013
$C_1\cdots C_3$	(2.664)	0.051	0.054	0.005	0.014
$C_2\cdots I$	(3.195)	0.045	0.051	0.002	0.004
$C_1\cdots I$	(4.655)	0.053	0.063	0.000_3	0.000_6
$O\cdots H$	(1.984)	0.098	0.099	0.012	0.027
$C_2\cdots H$	(2.208)	0.098	0.099	0.017	0.040
$C_3\cdots H$	(3.338)	0.108	0.111	0.012	0.031
$I\cdots H$	(5.279)	0.115	0.134	0.004	0.008
$C_2\cdots O$	(2.316)	0.057	0.063	0.004	0.011
$C_3\cdots O$	(3.433)	0.066	0.081	0.003	0.011
$I\cdots O$	(5.363)	0.068	0.109	0.000_1	0.000_4

DISCUSSION OF THE MEAN AMPLITUDES

All of the four molecules studied display very similar magnitudes of mean amplitudes for corresponding distance types. This feature might be expected *a priori* and supports the reliability of the analysis. The present results are

Table 5. Linear shrinkage effects (δ) for the halopropiolaldehydes CHOCCCl, CHOCCBr, and CHOCCI.

Molecule	Distance	δ, Å	
		$T=0$	298 K
CHOCCCl	$C_1\cdots C_3$	0.007	0.010
	$C_2\cdots Cl$	0.010	0.021
	$C_1\cdots Cl$	0.017	0.038
CHOCCBr	$C_1\cdots C_3$	0.007	0.011
	$C_2\cdots Br$	0.009	0.021
	$C_1\cdots Br$	0.016	0.038
CHOCCI	$C_1\cdots C_3$	0.007	0.011
	$C_2\cdots I$	0.009	0.019
	$C_1\cdots I$	0.016	0.038

Table 6. Mean amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) for propiolic acid chloride, CClOCCH.

Distance	(R, Å)	u, Å		K, Å	
		$T=0$	298 K	$T=0$	298 K
C_1-Cl	(1.789)	0.045	0.047	0.002	0.003
$C_1=O$	(1.192)	0.039	0.039	0.003	0.004
C_1-C_2	(1.426)	0.049	0.051	0.003	0.003
$C_2\equiv C_3$	(1.205)	0.036	0.036	0.007	0.014
C_3-H	(1.060)	0.074	0.074	0.033	0.046
$C_1\cdots C_3$	(2.631)	0.053	0.055	0.002	0.004
$C_2\cdots H$	(2.265)	0.079	0.079	0.022	0.040
$C_1\cdots H$	(3.691)	0.088	0.089	0.011	0.021
$O\cdots Cl$	(2.602)	0.055	0.063	0.000_7	0.002
$C_2\cdots Cl$	(2.683)	0.057	0.070	0.001	0.003
$C_3\cdots Cl$	(3.708)	0.076	0.116	0.000_4	0.000_7
$H\cdots Cl$	(4.681)	0.126	0.177	0.007	0.011
$C_2\cdots O$	(2.346)	0.054	0.056	0.002	0.004
$C_3\cdots O$	(3.482)	0.060	0.069	0.001	0.002
$H\cdots O$	(4.511)	0.102	0.115	0.008	0.014

Table 7. Linear shrinkage effects (δ) for propiolic acid chloride, CClOCCH.

Distance	δ, Å	
	$T=0$	298 K
$C_1\cdots C_3$	0.007	0.013
$C_2\cdots H$	0.018	0.020
$C_1\cdots H$	0.031	0.043

Table 8. Characteristic values of mean amplitudes at 298 K from the present calculations.

Distance type	u, Å
C – H(aldehyde)	0.080 – 0.081
C – H(ethynyl)	0.074
C≡C	0.036 – 0.037
C – C	0.050 – 0.051
C = O	0.039 – 0.042
$C_1 \cdots C_3$	0.053 – 0.055
$C_2 \cdots O$	0.06 – 0.07
$C_3 \cdots O$	0.07 – 0.08

very well consistent with the calculated mean amplitudes for propiolaldehyde (propynal) reported recently.[3]

Some of the characteristic values of mean amplitudes are listed in Table 8. Sugié *et al.*[3] have reported the calculated C – H(aldehyde) and C – H(ethynyl) mean amplitudes in CHOCCH at 20°C equal to 0.0797 Å and 0.0742 Å, respectively. These values are seen to be consistent with those listed in Table 8. This is also the case for [3] u(C≡C) = 0.0363 Å, and approximately for [3] u(C – C) = 0.0476 Å, u(C = O) = 0.0385 Å and $u(C_1 \cdots C_3) = 0.0513$ Å. For $u(C_2 \cdots O)$ in CHOCCH Sugié *et al.*[3] have calculated the value of 0.0572 Å (20°C) being similar to the present value of 0.056 Å (25°C) in CClOCCH. In the halopropiolaldehydes the corresponding values are slightly higher, *viz.* 0.063 – 0.066 Å. For $u(C_3 \cdots O)$ on the other hand Sugié *et al.*[3] give the relatively high value of 0.0858 Å (20°C), which is slightly above the characteristic value for the halopropiolaldehydes, *viz.* 0.081 – 0.082 Å at 25°C. In CClOCCH the corresponding value is somewhat lower, *viz.* 0.069 Å.

Sugié *et al.*[3] have deduced mean amplitudes of vibration for CHOCCH from electron diffraction data and found good agreement with the spectroscopic values. No electron diffraction mean amplitudes are available so far for the molecules of the present study.

REFERENCES

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