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GENERALIZED MEAN-SQUARE AMPLITUDES OF VIBRATION AND SHRINKAGE EFFECT IN LINEAR AND PLANAR AXYZ TYPE OF MOLECULES

K. VENKATESWARLU AND MISS V. MALATHY DEVI

Department of Physics, Kerala University, Alwaye-2

SPECTROSCOPIC calculations of mean amplitudes of vibration and shrinkage effects are of great interest in modern electron diffraction studies on gas molecules. In the present investigation, the theory of mean-square amplitudes of vibration is applied to four molecules of the linear AXYZ type and two molecules of planar AXYZ and their generalized mean-square amplitudes of vibration namely, parallel and perpendicular mean-square amplitudes and mean cross products at 300°K. are evaluated for all the bonded and non-bonded distance deviations.

The perpendicular mean-square amplitudes are determined by Morino's method.¹ The

molecular parameters, frequencies, and kinetic energy matrix elements are taken from references (2) and (3). The parallel mean-square amplitude values for these molecules have been evaluated earlier.⁴ The generalized mean-square amplitudes evaluated for linear and planar AXYZ molecules are reported in Tables I and II.

The deviation in the distance between two atoms from the sum of the distances between the atom pairs composing it is called the shrinkage effect. For linear AXYZ molecules, using the perpendicular mean-square amplitudes and by applying the theory developed by

TABLE I
Generalized mean-square amplitudes at 300°K. for linear AXYZ molecules (A²)

Bond	Mean-square amplitude	HN ₃	DN ₃	HNCO	HNCS
X - Y	$\langle(\Delta Z)^2\rangle$	0.001471	0.001478	0.001436	0.001412
	$\langle(\Delta X)^2\rangle$	0.003733	0.003135	0.001302	0.004549
	$\langle(\Delta Y)^2\rangle$	0.000777	0.000829	0.000917	0.001180
	$\langle(\Delta Z\Delta X)\rangle$	0.000312	-0.000253	-0.000031	-0.000032
Y - Z	$\langle(\Delta Z)^2\rangle$	0.001266	0.001272	0.001228	0.001586
	$\langle(\Delta X)^2\rangle$	0.004767	0.004590	0.003828	0.003435
	$\langle(\Delta Y)^2\rangle$	0.000825	0.000881	0.000887	0.000728
	$\langle(\Delta Z\Delta X)\rangle$	-0.000096	-0.00068	0.000003	0.000001
A - X	$\langle(\Delta Z)^2\rangle$	0.005526	0.004025	0.005503	0.005510
	$\langle(\Delta X)^2\rangle$	0.018194	0.012798	0.02288	0.027229
	$\langle(\Delta Y)^2\rangle$	0.000081	0.000087	0.000081	0.000125
	$\langle(\Delta Z\Delta X)\rangle$	-0.000587	-0.010353	-0.001104	-0.001499
X...Z	$\langle(\Delta Z)^2\rangle$	0.003048	0.003172	0.003164	0.003244
	$\langle(\Delta X)^2\rangle$	0.000161	0.000411	0.000202	0.000185
	$\langle(\Delta Y)^2\rangle$	0.000001	0.000001	0.000000	0.000342
	$\langle(\Delta Z\Delta X)\rangle$	-0.000174	-0.000150	-0.000033	-0.000057
A...Y	$\langle(\Delta Z)^2\rangle$	0.011190	0.009797	0.012170	0.012130
	$\langle(\Delta X)^2\rangle$	0.005061	0.004458	0.010456	0.013078
	$\langle(\Delta Y)^2\rangle$	0.000356	0.000380	0.000453	0.000537
	$\langle(\Delta Z\Delta X)\rangle$	-0.009681	-0.002563	-0.007808	-0.010446
A...Z	$\langle(\Delta Z)^2\rangle$	0.014750	0.013360	0.016650	0.017020
	$\langle(\Delta X)^2\rangle$	0.005771	0.005782	0.009339	0.011979
	$\langle(\Delta Y)^2\rangle$	0.000997	0.000104	0.000072	0.000114
	$\langle(\Delta Z\Delta X)\rangle$	-0.01126	0.000145	-0.004334	-0.006066

TABLE II
Generalized mean-square amplitudes (\AA^2)
for HCOF and DCOF

Bond	Mean-square amplitude	HCOF	DCOF
X-Z	$\langle(\Delta Z)^2\rangle$	0.001954	0.001954
	$\langle(\Delta X)^2\rangle$	0.002689	0.003270
	$\langle(\Delta Y)^2\rangle$	0.000501	0.000840
	$\langle(\Delta Z\Delta X)\rangle$	0.002347	0.004117
X-Y	$\langle(\Delta Z)^2\rangle$	0.001310	0.001312
	$\langle(\Delta X)^2\rangle$	0.001311	0.001290
	$\langle(\Delta Y)^2\rangle$	0.000601	0.001007
	$\langle(\Delta Z\Delta X)\rangle$	-0.000247	0.00008
A-X	$\langle(\Delta Z)^2\rangle$	0.006304	0.004434
	$\langle(\Delta X)^2\rangle$	0.006831	0.007502
	$\langle(\Delta Y)^2\rangle$	0.010030	0.005965
	$\langle(\Delta Z\Delta X)\rangle$	0.000401	0.002622
A...Z	$\langle(\Delta Z)^2\rangle$	0.008002	0.006898
	$\langle(\Delta X)^2\rangle$	0.006925	0.008904
	$\langle(\Delta Y)^2\rangle$	0.006052	0.002327
	$\langle(\Delta Z\Delta X)\rangle$	-0.000175	-0.003043
A...Y	$\langle(\Delta Z)^2\rangle$	0.007649	0.006103
	$\langle(\Delta X)^2\rangle$	0.007572	0.013129
	$\langle(\Delta Y)^2\rangle$	0.005722	0.002070
	$\langle(\Delta Z\Delta X)\rangle$	0.000634	0.004725
Y...Z	$\langle(\Delta Z)^2\rangle$	0.004386	0.004365
	$\langle(\Delta X)^2\rangle$	0.000195	0.000544
	$\langle(\Delta Y)^2\rangle$	0.000004	0.000007
	$\langle(\Delta Z\Delta X)\rangle$	-0.000612	-0.001196

Morino, the shrinkages for the linear part are calculated and the values obtained are reported in Table III.

TABLE III
Bastiansen-Morino shrinkage effect in linear AXYZ molecules

Molecule	Bond	Shrinkage (\AA)
HN ₃	N = N ≡ N	0.004251
DN ₃	N = N ≡ N	0.003923
HNCO	N = C = O	0.003718
HNCS	N = C = S	0.003558

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* *The Rose in India*. By B. P. Pal. (Indian Council of Agricultural Research), 1966. Pp. xviii + 265. Price Rs. 36.50 P.