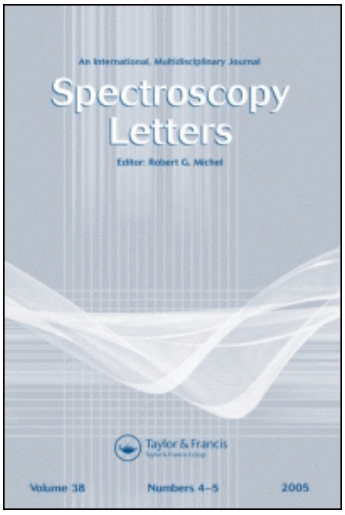

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Harmonic Force Fields and Mean Amplitudes For Gallium And Indium Trihalide Monomers

S. J. Cyvin[a]; A. Phongsatha[a]
[a] Division of Physical Chemistry, The University of Trondheim, Norway

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HARMONIC FORCE FIELDS AND MEAN AMPLITUDES FOR GALLIUM AND INDIUM TRIHALIDE MONOMERS

Keywords: Molecular vibrations, Force constants, Mean amplitudes, $GaCl_3$, $GaBr_3$, GaI_3, $InCl_3$, $InBr_3$, InI_3

S. J. Cyvin and A. Phongsatha*
Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway

ABSTRACT

Harmonic force fields (in-plane) for gallium and indium trihalides are developed from complete or incomplete experimental assignments of vibrational frequencies. The missing frequencies are predicted from the calculations Mean amplitudes of vibration are calculated.

INTRODUCTION

This is a continuation of systematic studies of harmonic force fields and mean amplitudes[1] for metal trihalide monomers. The molecules belong to the planar symmetrical (D_{3h}) model. Results from the similar studies of AlF_3,[2] $AlCl_3$,[3] $AlBr_3$,[4] and AlI_3[5] have been published. In the present work the GaX_3 and InX_3 (X = Cl, Br and I) molecules are treated. For two of them, viz. GaI_3 and $InBr_3$ the complete experimental assignment of in-plane frequencies is reported from Raman gas data.[6] These data are rather un-

*Visiting Research Scholar on the terms of NORAD Developing Aid Agency.

certain, especially for the ν_3 frequency. For the other molecules treated here this frequency is not given at all.

HARMONIC FORCE FIELDS

Gallium Triiodide and Indium Tribromide

For GaI_3 and $InBr_3$ the in-plane force constants were calculated by means of the values of ν_1, ν_3 and ν_4 from Beattie and Horder[6] and using the simple Urey-Bradley-Shimanouchi force field approximation.[3] The symmetry force constants[3] are given in Table 1 and the vibrational frequencies in Table 2.

For GaI_3 Morino et al.[7] have developed a valence force field using observed mean amplitudes from electron diffraction. The vibrational frequencies thus deduced prior to the spectroscopic observations[6] show a remarkably good agreement with the latter ones. They are[7] (in cm^{-1}): ν_1 = 150 ± 10, ν_3 = 300 ± 20 and ν_4 = 65 ± 10.

Gallium Trichloride and Tribromide, and Indium Trichloride and Triiodide

In the cases of $GaCl_3$, $GaBr_3$, $InCl_3$ and InI_3 the ν_3 frequency is unobserved. Hence an additional approximation is necessary. The following approach was followed, here illustrated for $GaCl_3$ as an example. (1) The f_{rr} value of -0.010 mdyne/A was assumed from analogy with the related

TABLE 1

In-Plane Symmetry Force Constants (mdyne/A)

Molecule	$F(A_1')$	$F_{11}(E')$	$F_{22}(E')$	$F_{12}(E')$
$GaCl_3$	3.047	3.076	0.081	0.006
$GaBr_3$	2.644	3.060	0.074	0.080
GaI_3	1.615	1.508	0.036	-0.021
$InCl_3$	2.558	2.457	0.047	-0.019
$InBr_3$	2.115	1.860	0.040	-0.049
InI_3	1.704	0.805	0.057	-0.173

TABLE 2

Vibrational Frequencies (cm^{-1})

Molecule	$\nu_1(A_1')$	$\nu_3(E')$	$\nu_4(E')$
$GaCl_3$	382	514[a]	128
$GaBr_3$	237[b]	439[a]	83
GaI_3	147	275	50
$InCl_3$	350	414[a]	94
$InBr_3$	212	280	62
InI_3	151	140[a]	44

[a] Calculated here. All other values are Raman gas data from Ref. 6.

[b] Subject to Fermi resonance.

molecules. It must be admitted that this approximation is rather uncertain. (2) With $F(A_1')$ = 3.047 mdyne/A obtained from ν_1 one obtains f_r = 3.067 mdyne/A, and consequently $F_{11}(E')$ = 3.076 mdyne/A. (3) The simple Urey-Bradley-Shimanouchi force field was assumed. (4) With these assumptions it is possible to calculate the rest of the in-plane symmetry force constants, viz. $F_{12}(E')$ = 0.006 mdyne/A and $F_{22}(E')$ = 0.081 mdyne/A. (5) This analysis also gives a predicted value of the missing frequency (ν_3).

The force constants are included in Table 1 and the vibrational frequencies in Table 2.

MEAN AMPLITUDES OF VIBRATION

The force constants were used to calculate the mean amplitudes of vibration[1] for the bonded and nonbonded distance in each of the molecules. The results for temperatures up to 2000 K are given in Table 3 (GaX_3) and Table 4 (InX_3).

For GaI_3 some mean amplitudes obtained by gas electron diffraction are available. Akishin et al.[8] have reported l(Ga-I) = 0.072 A and l(I···I) = 0.139 A. The more recent and accurate values due to Morino et al.[7] read l(Ga-I) =

TABLE 3

Mean Amplitudes of Vibration (A) for $GaCl_3$, $GaBr_3$ and GaI_3

Temp.(K)	Ga-Cl	Cl···Cl	Ga-Br	Br···Br	Ga-I	I···I
0	0.039	0.065	0.034	0.056	0.039	0.057
298	0.043	0.106	0.042	0.114	0.055	0.149
400	0.047	0.121	0.047	0.131	0.062	0.172
500	0.051	0.135	0.051	0.146	0.068	0.192
800	0.062	0.169	0.063	0.184	0.085	0.243
1000	0.068	0.189	0.070	0.206	0.095	0.272
2000	0.095	0.266	0.099	0.291	0.134	0.384

TABLE 4

Mean Amplitudes of Vibration (A) for $InCl_3$, $InBr_3$ and InI_3

Temp.(K)	In-Cl	Cl···Cl	In-Br	Br···Br	In-I	I···I
0	0.040	0.071	0.037	0.061	0.049	0.054
298	0.046	0.132	0.050	0.140	0.103	0.136
400	0.051	0.152	0.056	0.161	0.119	0.157
500	0.055	0.169	0.062	0.180	0.133	0.176
800	0.068	0.213	0.077	0.227	0.168	0.222
1000	0.076	0.238	0.086	0.254	0.188	0.248
2000	0.106	0.337	0.121	0.359	0.265	0.351

0.067 ± 0.004 A and l(I···I) = 0.163 ± 0.010 A at the temperature of 225 ± 30 °C. The latter set of values is seen to be very well compatible with the present calculations (Table 3).

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