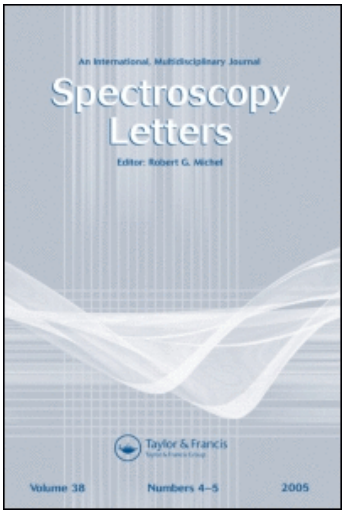

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Harmonic Force Field and Mean Amplitudes for Gallium Tribromide and Triiodide Dimers

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

To cite this Article Cyvin, S. J. and Phongsatha, A.(1975) 'Harmonic Force Field and Mean Amplitudes for Gallium Tribromide and Triiodide Dimers', Spectroscopy Letters, 8: 6, 405 — 411
To link to this Article: DOI: 10.1080/00387017508067341
URL: http://dx.doi.org/10.1080/00387017508067341

SPECTROSCOPY LETTERS, 8(6), 405-411 (1975)

HARMONIC FORCE FIELD AND MEAN AMPLITUDES FOR GALLIUM TRIBROMIDE AND TRIIODIDE DIMERS

Keywords: Molecular vibrations, Force constants, Mean amplitudes, Ga_2Br_6, Ga_2I_6

S. J. Cyvin and A. Phongsatha*

Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway

ABSTRACT

Harmonic force fields are developed for the Ga_2Br_6 and Ga_2I_6 molecules. The analysis confirms previous assignments of experimental frequencies. Mean amplitudes of vibration are calculated.

A previous communication[1] describes a normal coordinate analysis of Ga_2Cl_6 and contains references to the similar investigations of aluminum trihalide dimers published in this Journal. In the present work the same methods are applied to Ga_2Br_6 and Ga_2I_6 in order to contribute to the solution of the problem of vibrational assignments and to supply for the first time calculated mean amplitudes of vibration from spectroscopic data for these molecules.

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

STRUCTURE

Table 1 gives a survey of the structural parameters applied here along with those for Ga_2Cl_6. The data for the Cl and Br molecules are from gas electron diffraction measurements of Akishin et al.[2] Experimental data for Ga_2I_6 have not been found. For the bond distances we have adopted the values used by Beattie et al.[3] (given without reference), but not for the bond angles since their values for Ga_2Br_6 differ from the experimental data. Instead we transferred the values from Ga_2Br_6.

HARMONIC FORCE FIELD AND VIBRATIONAL ASSIGNMENT

A simple harmonic force field is based on five non-vanishing force constants. The numerical values are collected in Table 2 along with those for Ga_2Cl_6,[1] showing the regularities through the series of molecules in question.

The calculated frequencies from these simple force fields for Ga_2Br_6 and Ga_2I_6 are shown in Table 3 along with the observed values from the infrared (mull) and Raman (solid) data.[3] The calculations basically confirm the experimental assignments of the fundamentals throughout. It was found to be possible to adjust the force field to fit exactly all the observed frequencies within reasonable ranges of the force constants. These final

TABLE 1

Structural Parameters for Gallium Trihalide Dimers

Ga_2X_6	Ga_2Cl_6	Ga_2Br_6	Ga_2I_6
Ga-X(terminal), A	2.09	2.25	2.40
Ga-X(bridged), A	2.29	2.35	2.60
∠X(ter.)GaX(ter.), °	112	110	110
∠X(br.)GaX(br.), °	89	87	87

TABLE 2

Force Constants (mdyne/A) of Approximate Force Fields for Gallium Trihalide Dimers

Symbol	Ga_2Cl_6	Ga_2Br_6	Ga_2I_6
f_s	2.467	1.965	1.237
f_r	0.974	0.814	0.813
f_φ	0.180	0.180	0.160
f_t	0.320	0.270	0.200
f_τ	0.210	0.210	0.210

force fields are given in Table 4 and 5 for Ga_2Br_6 and Ga_2I_6, respectively. For the inactive $A_u(\nu_5)$ frequencies we have used the results from the approximate calculations. That was also done for the unobserved B_{3u} frequencies, viz. ν_{10} for both molecules and ν_9 for Ga_2I_6. Different calculated values for these frequencies are reported in Ref. 3, viz. ν_9 = 107 cm^{-1} (Ga_2I_6) and ν_{10} = 17 and 14 cm^{-1} for Ga_2Br_6 and Ga_2I_6, respectively.

MEAN AMPLITUDES OF VIBRATION

The final force fields were used to calculate the mean amplitudes of vibration.[4] The results are given in Tables 4 and 5 for Ga_2Br_6 and Ga_2I_6, respectively. For three of the distances, viz. Ga···X, X_b···X_t and cis (X···X), where X = Br or I, the values are given in parentheses because they depend critically on the particularly uncertain frequencies $\nu_5(A_u)$ and $\nu_{10}(B_{3u})$. This dependence is increasingly important with increasing temperature.

TABLE 3

Calculated and Observed Vibrational Frequencies (cm^{-1}) for Ga_2Br_6 and Ga_2I_6

Species	Ga_2Br_6		Ga_2I_6	
	Approx.	Final[a]	Approx.	Final[a]
A_g	304	291	245	229
	175	204	130	143
	120	119	86	85
	56	64	43	50
B_{1g}	128	158	95	68
B_{2g}	354	339	277	265
	111	74	82	55
B_{3g}	218	241	206	195
	127	85	99	64
A_u	68	(68)	52	(52)
B_{1u}	295	268	235	213
	160	188	119	134
	72	90	56	77
B_{2u}	236	232	217	189
	77	82	61	61
B_{3u}	371	347	300	273
	171	102	121	(121)
	37	(37)	30	(30)

[a]Calculated from the final force field and identical to the experimental data from Ref. 3. Parenthesized values are unobserved.

For Ga_2Br_6 a set of mean amplitudes from electron diffraction data have been reported.[2] They are presumably not accurate enough to be effectively useful in the force constant analysis. We are quoting the values here (in A units and the sequence of Table 4): 0.054, 0.054, 0.111, 0.080(ass.), 0.080, 0.080, 0.080, 0.120 and 0.128.

TABLE 4

Final Symmetry Force Constants (mdyne/A) for Ga_2Br_6

A_g	0.986						B_{1g}	0.273
	0.121	1.875						
	0.076	0.024	0.294					
	0.007	-0.015	-0.009	0.233				
B_{2g}	1.647				B_{3g}	0.789		
	-0.105	0.095				-0.140	0.127	
A_u	0.182				B_{1u}	1.021		
						0.290	1.864	
						-0.001	-0.034	0.283
B_{2u}	0.840				B_{3u}	1.419		
	0.030	0.191				-0.088	0.172	
						-0.113	-0.043	0.119

TABLE 5

Final Symmetry Force Constants (mdyne/A) for Ga_2I_6

A_g	0.882						B_{1g}	0.082
	0.119	0.191						
	0.046	0.017	0.206					
	0.025	-0.013	-0.004	0.214				
B_{2g}	0.968				B_{3g}	0.585		
	-0.094	0.093				-0.083	0.096	
A_u	0.163				B_{1u}	0.872		
						0.226	1.289	
						-0.002	-0.062	0.302
B_{2u}	0.695				B_{3u}	1.115		
	0.043	0.143				0.023	0.205	
						0.031	-0.007	0.151

TABLE 6

Calculated Mean Amplitudes of Vibration (A units) for Ga_2Br_6

Distance	0 K	298 K	500 K	1000 K
$Ga\text{-}Br_t$	0.040	0.055	0.068	0.095
$Ga\text{-}Br_b$	0.047	0.073	0.093	0.130
Ga···Br	(0.061)	(0.137)	(0.176)	(0.248)
Ga-Ga	0.050	0.083	0.105	0.147
$Br_b\cdots Br_b$	0.047	0.073	0.093	0.130
$Br_b\cdots Br_t$	(0.060)	(0.125)	(0.161)	(0.227)
com(Br···Br)	0.060	0.127	0.164	0.231
cis(Br···Br)	(0.084)	(0.245)	(0.317)	(0.448)
tr(Br···Br)	0.064	0.143	0.185	0.261

TABLE 7

Calculated Mean Amplitudes of Vibration (A units) for Ga_2I_6

Distance	0 K	298 K	500 K	1000 K
$Ga\text{-}I_t$	0.041	0.064	0.081	0.114
$Ga\text{-}I_b$	0.046	0.079	0.101	0.142
Ga···I	(0.059)	(0.143)	(0.185)	(0.261)
Ga-Ga	0.052	0.092	0.117	0.165
$I_b\cdots I_b$	0.045	0.084	0.108	0.152
$I_b\cdots I_t$	(0.056)	(0.133)	(0.172)	(0.243)
com(I···I)	0.056	0.131	0.170	0.239
cis(I···I)	(0.074)	(0.242)	(0.313)	(0.442)
tr(I···I)	0.062	0.160	0.207	0.292

REFERENCES

1 A. Phongsatha and S. J. Cyvin, Spectroscopy Letters (in press).

2 P. A. Akishin, V. A. Naumov and V. M. Tatevskii, Kristallografiya 4, 194 (1959).

3 I. R. Beattie, T. Gilson and G. A. Ozin, J. Chem. Soc. (A), 813 (1968).

4 S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Elsevier, Amsterdam / Universitetsforlaget, Oslo, 1968.

Received March 21, 1975
Accepted April 11, 1975