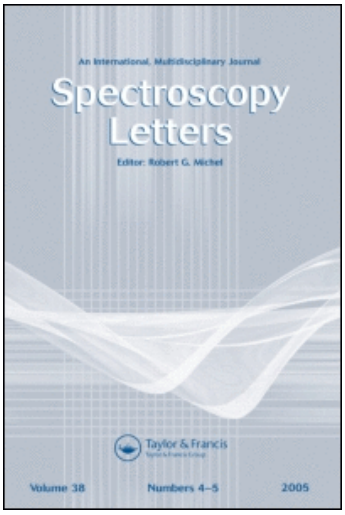

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HARMONIC FORCE FIELD AND MEAN AMPLITUDES FOR GALLIUM TRICHLORIDE DIMER

Keywords: Molecular vibrations, Force constants, Mean amplitudes, Ga_2Cl_6

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ABSTRACT

A harmonic force field is developed and an assignment of the vibrational frequencies for Ga_2Cl_6 is proposed. The mean amplitudes of vibration are calculated.

INTRODUCTION

The purpose of this work is to investigate the harmonic force field for Ga_2Cl_6 with calculations of the mean amplitudes of vibration.[1] The molecule is known to belong to the bridged diborane-like model (symmetry D_{2h}). Many works on molecules belonging to this model have been published. The present work is a continuation of the similar analyses of aluminum trihalide dimers.[2-6] Several spectroscopic investigations on gallium trihalide dimers have been reported.[7-9] Additional references are found in the excellent thesis recently published by Rytter.[10] In conclusion it must be admitted that the assignments of

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fundamental frequencies for these molecules still contain several uncertain points.

STRUCTURE

The bridged structure (D_{2h}) with a planar ring was verified for Ga_2Cl_6 by Akishin et al.[11] in their gas electron diffraction investigation. We have adopted the structural parameters from that work, viz. Ga-Cl(terminal) = 2.09 A, Ga-Cl(bridged) = 2.29 A, ∠ Cl(ter.)GaCl (ter.) = 112° and ∠ Cl(br.)GaCl(br.) = 89°.

HARMONIC FORCE FIELD AND VIBRATIONAL ASSIGNMENT

In the first calculation a simple harmonic force field was derived within the approximation of a diagonal F matrix based on symmetry coordinates.[12,13] In this respect the approximate force field is of the same kind as was applied to Al_2F_6.[4] The five nonvanishing force constants (in mdyne/A) are: f_s(terminal Ga-Cl) = 2.467, f_r(bridged Ga-Cl) = 0.974, f_φ = 0.18, f_t = 0.32 and f_τ = 0.21. The calculated frequencies from this force field are shown in Table 1. Different values of the force constants were tried in order to improve the agreement with the observed frequencies[7-9] quoted in Table 1. Especially was the effect of f_φ investigated. Several frequencies improved while others got worse when using values of f_φ above and below 0.18 mdyne/A. Hence the value chosen here arises from a compromise.

A refined force field was produced with the aid of the observed Raman and infrared data[7-9] quoted in Table 1. The final force constants in terms of symmetry coordinates[13,14] are shown in Table 2, and the corresponding frequencies are included in Table 1. Most of these frequencies are seen to be identical with the observed values (cf. Table 1). The experimental data are from Beattie et al.[7]: most of the Raman data from melts, mull infrared data, but including a few solid-state frequencies. This selection of experimental values was taken from the quotation of Adams et al.[14]

TABLE 1

Calculated and Observed Vibrational Frequencies (cm^{-1}) for Ga_2Cl_6

Species	Calculated		Observed	
	Approx.	Final	Raman	Infrared
A_g	409	413	413	-
	279	318	318	-
	162	167	167	-
	85	100	100	-
B_{1g}	192	215	215	-
B_{2g}	462	462	462	-
	150	117	117	-
B_{3g}	271	243	243	-
	179	125	125	-
A_u	105	106	-	-
B_{1u}	407	390	-	390
	251	282	-	282
	103	156	-	156
B_{2u}	300	318	-	318
	119	114	-	114
B_{3u}	473	464	-	464
	255	203	-	-
	57	80	-	-

For the unobserved frequency of $A_u(\nu_5)$ we have calculated 105 cm^{-1} from the approximate force field. It agrees nicely with the calculated value of 106 cm^{-1} from Ref. 14. Beattie et al.[8] have suggested the re-assignment $\nu_{12}(B_{2g})$ = 104 cm^{-1} and $\nu_{15}(B_{1g})$ = 117 cm^{-1}, while 215 cm^{-1} should be explained as a combination band. Our calculations do not confirm this re-assignment. We therefore prefer to use 215 cm^{-1} and 117 cm^{-1} as $\nu_{15}(B_{1g})$ and ν_{12} (B_{2g}), respectively, in accord with Adams et al.[14] and the original assignment of Beattie et al.[7] For $\nu_9(B_{3u})$ no experimental value is quoted in Ref. 14. We have chosen 203 cm^{-1} as the calculated value from the same work.[14]

However, Beattie et al.[7] do report a gas infrared frequency of $\nu_9(B_{3u}) = 202\ cm^{-1}$.

After completion of the present calculations Rytter[10] presented a tentative assignment of the Raman-active fundamentals of Ga_2Cl_6. It is mainly based on new melt data[10] and therefore of interest to be quoted here. The B_{3g} frequencies are solid bands from literature. All values in cm^{-1};

A_g: 410(s)p, 339(m)p, 165(m)p, 96(vs)
B_{1g}: 109(w)
B_{2g}: 462(w), 128(w)
B_{3g}: 347, 117

The assignments of the B modes are substantially different from ours (Table 1). Rytter's assignment is not supported by force constant calculations, as the author points out himself.[10]

MEAN AMPLITUDES OF VIBRATION

The developed force field (Table 2) was used to calculate the mean amplitudes of vibration.[1] The results are shown in Table 3.

Akishin et al.[11] have published a set of mean amplitudes for Ga_2Cl_6 from electron diffraction data. These values are presumably not accurate enough to be effectively useful in the force constant analysis. They are (in A units and the sequence of Table 3): 0.049, 0.049, 0.116, 0.076(ass.), 0.066, 0.076, 0.076, 0.090 and 0.097.

TABLE 2

Final Symmetry Force Constants (mdyne/A) for Ga_2Cl_6

A_g	1.105				B_{1g}	0.226	
	0.054	2.531					
	0.056	0.009	0.366				
	0.018	-0.004	-0.008	0.244			
B_{2g}	2.407			B_{3g}	0.760		
	-0.064	0.115			-0.033	0.092	
A_u	0.183			B_{1u}	1.215		
					0.169	2.359	
					-0.055	-0.058	0.407
B_{2u}	1.041			B_{3u}	2.263		
	-0.040	0.175			-0.059	0.324	
					-0.056	-0.118	0.200

TABLE 3

Calculated Mean Amplitudes of Vibration (A units) for Ga_2Cl_6

Distance	0 K	298 K	500 K	1000 K
$Ga\text{-}Cl_t$	0.041	0.048	0.057	0.077
$Ga\text{-}Cl_b$	0.051	0.069	0.086	0.119
Ga···Cl	0.064	0.115	0.147	0.206
Ga-Ga	0.048	0.074	0.094	0.131
$Cl_b\cdots Cl_b$	0.056	0.071	0.088	0.121
$Cl_b\cdots Cl_t$	0.070	0.115	0.146	0.205
com(Cl···Cl)	0.069	0.114	0.145	0.203
cis(Cl···Cl)	0.091	0.192	0.247	0.348
tr(Cl···Cl)	0.072	0.128	0.163	0.229

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