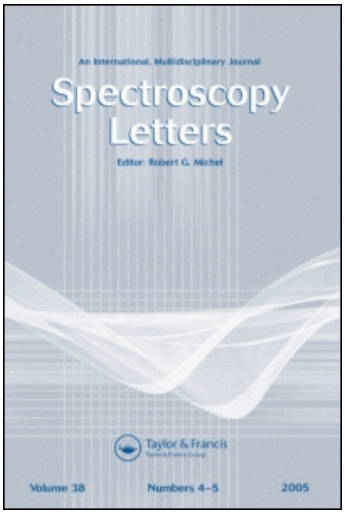

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Phongsatha, A. and Cyvin, S. J.(1974) 'Harmonic Forge Fields And Mean Amplitudes For Aluminum Tribromide Dimer And Monomer', Spectroscopy Letters, 7: 8, 365 — 370
To link to this Article: DOI: 10.1080/00387017408067259
URL: http://dx.doi.org/10.1080/00387017408067259

SPECTROSCOPY LETTERS, 7(8), 365-370 (1974)

HARMONIC FORCE FIELDS AND MEAN AMPLITUDES FOR ALUMINUM TRIBROMIDE DIMER AND MONOMER

Keywords: Molecular vibrations, Force constants, Mean amplitudes, Al_2Br_6, $AlBr_3$

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ABSTRACT

Harmonic force fields for $AlBr_3$ and Al_2Br_6 are developed. The vibrational assignment for the latter molecule is discussed. Calculated mean amplitudes for both molecules are reported.

INTRODUCTION

Systematic studies of harmonic force fields and mean amplitudes for aluminum trihalide monomers and dimers are in progress. Some results have been reported previously for AlF_3,[1] Al_2F_6,[1] $AlCl_3$,[2,3] and Al_2Cl_6.[4,5] In the present work the Al_2Br_6 and $AlBr_3$ molecules are treated. The dimer has been investigated by gas electron diffraction.[6] Several reports on the vibrational spectrum of Al_2Br_6 are available,[7-10] but the existing assignments of fundamental frequencies are all incomplete and contain several uncertain features. In one of the works[9] a partial assignment

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Financial support to A.P. from Norwegian Agency for International Development (NORAD) is gratefully acknowledged.

of the $AlBr_3$ fundamentals is presented.

ALUMINUM TRIBROMIDE DIMER

The bridged structure (D_{2h}) with a planar ring has been found for Al_2Br_6 by Akishin et al.[6] in their gas electron diffraction investigation. We have adopted the structural parameters from that work, viz. Al-Br(terminal) = 2.22 Å, Al-Br(bridged) = 2.38 Å, ∠ Br(ter.)AlBr(ter.) = 118°, ∠ Br(br.)AlBr(br.) = 82°.

In a preliminary analysis a simplified force field for Al_2Cl_6 [4] was trasferred to the molecule in question. Then the force constants were adjusted to fit some of the observed frequencies available in order to get a guide for setting up a new approximate force field. Thus a simple harmonic force field was derived within the approximation of a diagonal F matrix based on symmetry coordinates.[3,11] In this respect the approximate force field is of the same kind as was applied to Al_2F_6.[1] The five nonvanishing force constants (in mdyne/Å) are: f_s(terminal Al-Br) = 1.7, f_r (bridged Al-Br) = 1.2, f_φ = 0.2, f_t = 0.29 and f_τ = 0.23. The calculated frequencies from this approximate force field are shown in Table 1.

A refined force field was produced with the aid of observed frequencies. The Raman data quoted in Table 1 are from the investigations of melt systems by Beattie et al.,[7] which were basically confirmed by Begun et al.[10] These measurements are more complete than the corresponding Raman gas data,[9] and the frequency shifts from melt to gas were found to be small in general. The infrared frequencies quoted in Table 1 are the Nujon mull data from Beattie et al.[7] All these experimental frequencies with one notable exception were used in the present refined calculations. For the low frequency in B_{3g} (ν_7) we used 140 cm^{-1} (equal to ν_3) rather than the reported experimental value of 81 cm^{-1}. It was not succeeded to reproduce the latter value with reasonable force constants, and a misassignment in the experimental work cannot be outruled. For the unobserved

TABLE 1

Calculated and Observed Vibrational Frequencies (cm^{-1}) for Al_2Br_6

Species*	Calculated		Observed[7]	
	Approx.	Refined	Raman	Infrared
A_g	445	409	409	-
	192	210	210	-
	140	140	140	-
	64	67	67	-
B_{1g}	135	135	-	-
B_{2g}	515	489	489	-
	120	114	114	-
B_{3g}	362	340	340	-
	140	140	81	-
A_u	68	68	-	-
B_{1u}	424	375	-	375
	183	198	-	198
	88	111	-	111
B_{2u}	369	345	-	345
	86	90	-	90
B_{3u}	547	502	-	502
	174	174	-	-
	41	41	-	-

* The designations B_{1g}/B_{3g} and B_{1u}/B_{3u} follow the conventions adopted in Refs. 1, 3 and 11.

frequency of B_{1g} (ν_{15}) we have calculated 135 cm^{-1}, which is comparable to the calculated value 103 cm^{-1} in Ref. 7. This is also true for the middle frequency of B_{3u} (ν_9), for which the calculated values are 174 and 162 cm^{-1} here and in Ref. 7, respectively. The lowest B_{3u} frequency (ν_{10}) is to be described as the out-of-plane ring deformation,[8] for which the present approximate calculation (41 cm^{-1}) is very uncertain. We have therefore used the value 18 cm^{-1} from Ref. 7 as an alternative for ν_{10} in the subsequent computations of mean amplitudes.

The refined force field is presented in Table 2 in

TABLE 2

Final Symmetry Force Constants (mdyne/Å) for Al_2Br_6

A_g	1.22				B_{1g}	0.20
	0.18	1.67				
	0.06	0.01	0.30			
	0.01	-0.02	-0.01	0.21		
B_{2g}	1.53			B_{3g}	1.11	
	0.00	0.18			0.03	0.19
A_u	0.20		B_{1u}	1.15		
				0.26	1.74	
				0.04	-0.07	0.31
B_{2u}	1.15		B_{3u}	1.54		
	0.05	0.20		0.03	0.22	
				0.04	-0.00	0.19

terms of the F matrix based on symmetry coordinates.[3,11] The complete set of the corresponding frequencies is included in Table 1.

The developed force field was used to calculate the mean amplitudes of vibration.[12] The results are given in Table 3. The types of the interatomic distances are identi-

TABLE 3

Calculated Mean Amplitudes of Vibration (Å units) for Al_2Br_6

Distance	0 K	298 K	500 K	1000 K
Al-Br_t	0.046	0.057	0.069	0.094
Al-Br_b	0.050	0.065	0.081	0.111
Al···Br	0.063 [0.068][a]	0.122 [0.182]	0.156 [0.234]	0.219 [0.331]
Al-Al	0.060	0.080	0.099	0.137
Br_b···Br_b	0.047	0.073	0.093	0.130
Br_b···Br_t	0.054 [0.055]	0.101 [0.106]	0.129 [0.136]	0.182 [0.191]
com(Br···Br)	0.057	0.110	0.141	0.198
cis(Br···Br)	0.081 [0.105]	0.229 [0.446]	0.296 [0.577]	0.418 [0.816]
trans(Br···Br)	0.059	0.119	0.153	0.215

[a] Values in brackets are consistent with ν_{10} = 18 cm^{-1} instead of 41 cm^{-1}.

fied in accord with previous reports.[1,5] The mean amplitudes for three of the distances depend significantly on the ν_{10} frequency. The table shows the results of the calculations using both ν_{10} = 41 cm^{-1} and [in brackets] ν_{10} = 18 cm^{-1}. The mean amplitude values reported from electron diffraction data[6] are only rudimentary and seem to be highly inaccurate. They are not believed to be helpful as additional information in the force constant determination.

ALUMINUM TRIBROMIDE MONOMER

The observed fundamentals of in-plane vibrations (ν_1 = 228, ν_3 = 360, ν_4 = 93 cm^{-1})[9] make it feasible to establish a harmonic in-plane force field for this molecule. We obtained the results from two different approaches using (a) the L-approximation method and (b) the simple Urey-Bradley-Shimanouchi force field approximation. The results are $F(A_1')$ = 2.447 mdyne/Å and (a) $F_{11}(E')$ = 1.270, $F_{12}(E')$ = -0.106, $F_{22}(E')$ = 0.0747 mdyne/Å for $L_{12}(E')$ = 0; (b) $F_{11}(E')$ = 1.482, $F_{12}(E')$ = -0.186, $F_{22}(E')$ = 0.0798 mdyne/Å for the Urey-Bradley-Shimanouchi force field.[3] The mean amplitudes of vibration[12] were calculated with both of the force fields. The latter ones (b) are shown in Table 4; we believe that the Urey-Bradley-Shimanouchi force field is the

TABLE 4

Mean Amplitudes of Vibration (Å) for $AlBr_3$

Temp. (K)	Al-Br	Br···Br
0	0.049_6	0.054_5
298	0.061_8	0.104_1
400	0.068_9	0.119_8
500	0.075_6	0.133_5
600	0.082_0	0.146_0
800	0.093_6	0.168_3
1000	0.104_2	0.188_0
1500	0.126_9	0.230_1
2000	0.146_3	0.265_6

better one of the two approximations applied. However, the mean amplitudes do not differ much from those of the L-matrix approximation method (a). One has, for instance, from the force field (a): $l(Al\text{-}Br) = 0.049_3$, $l(Br\cdots Br) = 0.055_1$ Å at absolute zero, and the values 0.101_4 and 0.191_7 Å at 1000 K.

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Received June 8, 1974
Accepted June 17, 1974