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Vibrational Analysis of Nb_2Br_{10} and Ta_2Br_{10}: Harmonic Force Field and Mean Amplitudes

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Normal coordinate analyses for Nb_2Br_{10} and Ta_2Br_{10} are performed. The final force constants are given in terms of symmetry coordinates. Assignments of vibrational frequencies are given along with the corresponding potential energy distributions. Calculated mean amplitudes of vibration for the bonded distances are reported.

Introduction

This is a continuation of our vibrational studies of some metal pentahalide dimers. The analysis of Nb_2Cl_{10} and Ta_2Cl_{10} [1] is followed up by similar studies of the corresponding bromides. This approach seems to be warranted for several reasons. Firstly, it is supposed to give a useful check of the experimental assignments of the vibrational frequencies. Secondly, it may lead to a complete harmonic force field on a relatively firm basis. Only a few papers on Nb_2Br_{10} and Ta_2Br_{10} [2, 3] in this direction are available so far and they may certainly be improved. Finally, a force field developed in the course of this analysis may be useful for calculations of various molecular constants. In the present work the application to calculations of mean amplitudes of vibration is reported.

Normal Coordinate Analysis

Molecular Structure

The niobium and tantalum pentabromides belong to a group of compounds which crystallize as dimers, Nb_2Br_{10} and Ta_2Br_{10}, in which each unit consists of a central atom surrounded by the halogen atoms at the corners of a more or less distorted octahedron[4, 5]. Accurate values for bond distances and valence bond angles have not been measured. It has been deduced from NQR experiments[6] that the intradimeric angle between the bridging bonds decreases through the series of halogens Cl, Br and I in that order. Its value remains, however, between the limits of 97 and 102°. These relatively small changes are not expected to have significant influence on the normal coordinate analysis; we have therefore chosen this angle to be the same in Nb_2Br_{10} and Ta_2Br_{10} as in the corresponding chlorides[1], viz. 101.3°. The same value was adopted in the NQR work[6]. All the external Br—metal—Br angles were assumed to be 90°. In order to estimate the bond lengths it was assumed that they change by the same ratio when going from chloride to bromide as in the monomeric molecules. It is reported for the monomeric pentahalides from a gas electron diffraction investigation[7]: Nb—Cl = 2.29 Å, Nb—Br = 2.45 Å, Ta—Cl = 2.30 Å and Ta—Br = 2.46 Å. The estimated bond lengths for the dimeric molecules in question are collected in Table 1.

Table 1. *Estimated Bond Lengths (in Å) for* Nb_2Br_{10} *and* Ta_2Br_{10}

M_2Br_{10}	Nb_2Br_{10}	Ta_2Br_{10}
R (equatorial *M*—Br)	2.42	2.42
D (bridged *M*—Br)	2.75	2.75
T (axial *M*—Br)	2.47	2.47

Symmetry Coordinates

The double-octahedron model for the dimeric molecules in question has the symmetry of D_{2h}. The normal modes of vibration are distributed among the symmetry species according to

$$\Gamma_{vib} = 6\,A_g + 2\,B_{1g} + 3\,B_{2g} + 4\,B_{3g} + 2\,A_u + 5\,B_{1u} + 4\,B_{2u} + 4\,B_{3u}.$$

This species notation depends on the choice of the cartesian axes; it conforms with the conventions adopted in Ref. [2].

We believe that the specification of the chosen set of internal coordinates is essentially important when a force field is presented. In the present work we adher to a set of symmetry coordinates as the basis of the force-constant matrix. A detailed account of the symmetry coordinates is found in Ref. [1].

Force Constants

Following the same approach as applied to Nb_2Cl_{10}[1] an initial force field for Nb_2Br_{10} was constructed on the basis of valence coordinates with redundancies. Also the numerical values from Nb_2Cl_{10} were transferred to Nb_2Br_{10} except for the three stretching force constants. They were reduced by a ratio taken from the analogy with $VOCl_3$ and $VOBr_3$[8]. In conclusion this initial force field is given by

$$f_r = 1.5;\ f_t = 1.75;\ f_d = 0.75;\ f_\alpha = 0.005;\ f_\tau = 0.03;\ f_\beta = f_\gamma = f_\delta = f_\varepsilon = f_\varphi = 0.12.$$

All values are in mdyne/Å, and the notation from Ref. [1] is adopted. A refined force field for Nb_2Br_{10} was produced with the aid of experi-

Table 2. *Final Symmetry Force Constants (mdyne/Å) for* Nb_2Br_{10}

A_g	1.612					
	0.000	2.320				
	0.027	0.000	0.774			
	0.012	0.000	−0.016	0.216		
	−0.027	0.000	−0.045	−0.125	0.295	
	0.036	0.000	0.022	0.038	−0.019	0.281
B_{1g}	0.148					
	0.006	0.158				
B_{2g}	1.145					
	0.040	0.120				
	−0.003	−0.004	0.078			
B_{3g}	1.393					
	−0.048	0.746				
	0.018	0.018	0.110			
	0.034	−0.011	0.026	0.196		
A_u	0.120					
	0.001	0.119				
B_{1u}	1.308					
	0.000	2.299				
	0.062	0.000	0.891			
	−0.040	0.000	−0.128	0.318		
	0.030	0.000	0.019	−0.047	0.244	
B_{2u}	1.334					
	−0.031	0.802				
	0.020	0.025	0.128			
	0.052	0.058	−0.007	0.305		
B_{3u}	1.200					
	0.050	0.130				
	0.019	−0.006	0.103			
	0.010	−0.001	0.002	0.026		

mental data of vibrational frequencies (see below). The force constants in terms of symmetry coordinates[1] are shown in Table 2.

The final force constants of Nb_2Br_{10} (Table 2) were transferred to Ta_2Br_{10} as the initial approximate set for the latter molecule. Again a refined force field was produced with the aid of experimental frequencies, and the final force constants are shown in Table 3.

Table 3. *Final Symmetry Force Constants (mdyne/Å) for* Ta_2Br_{10}

A_g	1.973					
	0.000	2.340				
	— 0.043	0.000	0.830			
	0.015	0.000	— 0.005	0.236		
	— 0.017	0.000	— 0.066	— 0.127	0.289	
	0.032	0.000	0.027	0.065	— 0.042	0.317
B_{1g}	0.131					
	0.015	0.154				
B_{2g}	1.444					
	0.013	0.097				
	— 0.011	0.000_3	0.082			
B_{3g}	1.636					
	0.010	0.744				
	0.020	0.012	0.121			
	0.032	— 0.012	0.036	0.215		
A_u	0.113					
	0.000_1	0.113				
B_{1u}	1.659					
	0.000	2.257				
	— 0.082	0.000	1.041			
	— 0.026	0.000	— 0.163	0.356		
	0.003	0.000	0.009	— 0.023	0.294	
B_{2u}	1.775					
	0.052	0.866				
	— 0.007	0.009	0.133			
	0.026	0.049	— 0.004	0.312		
B_{3u}	1.568					
	0.029	0.123				
	0.000_0	— 0.004	0.104			
	— 0.003	— 0.000_4	0.001	0.026		

Vibrational Frequencies

For a molecule belonging to the model considered here it is predicted by group-theoretical methods that 15 out of the 30 fundamentals

Table 4. *Calculated and Observed Frequencies* (cm^{-1}) *along with the Potential Energy Distribution for* Nb_2Br_{10}

Species	Approx.	Final[a]	Potential energy distribution[b]
A_g	287	291	$67\ S_1 + 19\ S_3$
	193	222	$100\ S_2$
	155	167	$46\ S_3 + 26\ S_5 + 21\ S_4 + 18\ S_1$
	114	124	$46\ S_4 + 34\ S_6$
	85	78	$73\ S_5$
	54	49	$65\ S_4 + 43\ S_6 + 32\ S_5 + 28\ S_3$
B_{1g}	112	130	$79\ S_2 + 18\ S_1$
	81	89	$82\ S_1 + 21\ S_2$
B_{2g}	336	267	$92\ S_1$
	102	103	$92\ S_2$
	77	62	$95\ S_3$
B_{3g}	279	261	$74\ S_1 + 17\ S_2$
	151	153	$78\ S_2$
	110	114	$42\ S_3 + 27\ S_4$
	63	53	$68\ S_4 + 51\ S_3$
A_u	93	93	$87\ S_1$
	37	37	$88\ S_2$
B_{1u}	294	265	$60\ S_1 + 36\ S_3$
	193	221	$100\ S_2$
	166	159	$64\ S_3 + 34\ S_1$
	110	115	$57\ S_4 + 24\ S_5$
	82	71	$68\ S_5 + 39\ S_4$
B_{2u}	283	257	$70\ S_1 + 20\ S_2$
	149	148	$48\ S_2 + 30\ S_1 + 20\ S_3$
	83	98	$81\ S_4$
	50	53	$66\ S_3 + 25\ S_2$
B_{3u}	342	273	$91\ S_1$
	140	129	$65\ S_3 + 26\ S_4$
	103	109	$88\ S_2$
	28	26	$69\ S_4 + 26\ S_3$

[a] Most of the values are equal to observed frequencies; see the text.
[b] Terms below 15 are omitted.

should be Raman-active ($6\ A_g + 2\ B_{1g} + 3\ B_{2g} + 4\ B_{3g}$) and 13 infrared-active ($5\ B_{1u} + 4\ B_{2u} + 4\ B_{3u}$). In addition there are 2 fundamentals ($2\ A_u$) inactive in both infrared and Raman.

From the experimental results of *Beattie* et al.[2] and *Vu-Thi Ngoc-Trâm*[3] the 15 Raman-active fundamentals were deduced. One fre-

Table 5. *Calculated and Observed Frequencies* (cm^{-1}) *along with the Potential Energy Distribution for* Ta_2Br_{10}

Species	Approx.	Final[a]	Potential energy distribution[b]
A_g	237	266	79 S_1
	222	223	100 S_2
	166	170	50 S_3 + 27 S_5 + 26 S_4
	116	126	41 S_6 + 36 S_4
	78	75	75 S_5 + 20 S_6
	47	48	73 S_4 + 39 S_6 + 32 S_3 + 31 S_5
B_{1g}	130	130	77 S_2 + 16 S_1
	89	82	86 S_1 + 24 S_2
B_{2g}	217	247	94 S_1
	101	90	95 S_2
	58	60	96 S_3
B_{3g}	215	236	85 S_1
	152	150	86 S_2
	105	112	41 S_3 + 33 S_4
	53	54	68 S_4 + 56 S_3
A_u	93	90	87 S_1
	37	36	88 S_2
B_{1u}	221	255	64 S_1 + 26 S_3
	216	219	100 S_2
	158	163	78 S_3 + 33 S_1 + 15 S_4
	110	113	61 S_4 + 29 S_5
	71	81	65 S_5 + 32 S_4
B_{2u}	212	252	78 S_1
	145	150	59 S_2 + 24 S_3 + 22 S_1
	95	96	89 S_4
	53	53	69 S_3 + 26 S_2
B_{3u}	221	258	93 S_1
	128	128	69 S_3 + 26 S_4
	106	103	92 S_2
	26	26	68 S_4 + 26 S_3

[a] See footnotes to Table 4.
[b] See footnotes to Table 4.

quency from the latter author[3] was omitted as it did not fit into the set of approximate frequencies (see Table 4) calculated with our initial force field. It is considered permissible to omit this frequency especially because it was not recorded by other workers[2]. The only infrared data available for Nb_2Br_{10} are due to *Beattie* et al.[2], who have recorded 12 fundamentals, missing one. All the observed fundamentals were used in the refinement of the force field. The missing infrared-active frequency along with the two inactive frequencies were estimated on the basis of the approximate calculations. Table 4 includes the complete set of assigned frequencies for Nb_2Br_{10} consistent with the final force field of Table 2.

The work of *Beattie* et al.[2] includes 14 Raman-active and 11 infrared-active fundamentals for Ta_2Br_{10} as the only source of experimental frequencies available for this molecule. We have again estimated the missing frequencies from the approximate calculations and used them along with the observed frequencies in the refinement of the force field. The calculated frequencies from the initial and final force fields are given in Table 5.

Potential Energy Distribution

The potential energy distributions for Nb_2Br_{10} and Ta_2Br_{10} were calculated from the final force fields. The results are included in Tables 4 and 5, resp.

Discussion

The approximation of a valence force field showed to give very good initial values of vibrational frequencies for Nb_2Br_{10} when compared with the experimental data. In addition to a general qualitative agreement through the whole range of frequencies we found quantitative agreements within a few wave numbers in many cases. This may seem surprising and especially gratifying in view of the great simplicity of the approximate force field. Also the initial force field for Ta_2Br_{10} with force constants transferred from Nb_2Br_{10} showed to be successful. In conclusion no substantial difficulties were encountered in the assignment of the frequencies.

Mean Amplitudes of Vibration

The final force fields were used to calculate the mean amplitudes of vibration[9] for the two molecules in question. Results for the bonded

Table 6. *Mean Amplitudes of Vibration (A Units) for the Bond Distances in* Nb_2Br_{10} *and* Ta_2Br_{10}

M_2Br_{10}	Nb_2Br_{10}		Ta_2Br_{10}	
Temperature	0 K	298 K	0 K	298 K
M—Br (equatorial)	0.040	0.057	0.036	0.051
M—Br (axial)	0.040	0.055	0.036	0.050
M—Br (bridged)	0.045	0.075	0.042	0.072

interatomic distances are given in Table 6. The values display the same characteristics as were found and discussed in the case of Nb_2Cl_{10} and Ta_2Cl_{10} [1].

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