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VIBRATIONAL ANALYSIS OF $TaBr_5$

By

E.M. NOUR

Department of Chemistry, Qatar University, Doha

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ABSTRACT

Vibrational analysis for $TaBr_5$ is achieved on the basis of D_{3h} symmetry and employing the GF matrix method. Each vibration is quantitatively assigned according to the calculated values of the potential energy distributions. The force constant values are calculated. These indicate the weakness of the axial Ta–Br bonds (165 Nm^{-1}) compared with the equatorial Ta–Br (261 Nm^{-1}). The $2A_2''$ (ν_3 and ν_4) and E′ (ν_5) which were not experimentally observed are calculated at 263, 89, and 308 cm^{-1}, respectively.

INTRODUCTION

Most of the solid pentahalide metal complexes exist as dimers or tetramers. The monomeric species could only exist in pure form in the gas phase or in dilute solutions or possibly isolated in inert matrices at low temperature. Despite the large number of studies on many pentahalides, there are wide uncertainties regrarding the vibarational assignments of these species (Zalkin and Sands, 1958; Werder *et al,* 1967; Beattie and Ozin, 1969; Selig *et al,* 1970; Acquista and Abramowitz, 1973; Hagen *et al,* 1982; and Nunziante–Cesaro *et al,* 1984). These mainly arise from the overlap between the bands of the monomer with those of the dimer or tetramer .

In a previous communication (Nour, 1986) full normal coordinate analysis including the determination of the potential energy distribution values for all modes are described for the penta–halides $NbCl_5$, $NbBr_5$, MoF_5 and $MoCl_5$ under D_{3h} symmetry. These calculations enabled us to obtain more acceptable vibarational assignments for these species.

Structural study (Wells, 1975) on $TaBr_5$ showed that the species exists in the solid state as Ta_2Br_{10} dimer. On the other hand vibrational work (Walton and Brisdon, 1967 and Beattie and Ozin, 1969) indicated that the $TaBr_5$ monomer belongs to the trigonal bipyramidal structure with D_{3h} symmetry. In this study we present a complete vibrational analysis for $TaBr_5$. All modes are quantitatively assigned and the values of all force constants are determined. These values are discussed in comparision with those reported for related pentahalides.

RESULTS AND DISCUSSION

The vibarational modes of $TaBr_5$ under D_{3h} symmetry are distributed between 4 monodegenerates of type $2A'_1$ and $2A''_2$ and 4 doubly degenerates, 3E' and E''. The A'_1, E' and E'' modes are Raman active while the A''_2 and E'' are infrared active. The axial Ta−Br' bond stretches have the A'_1 and A''_2 characters and the equatorial Ta−Br stretches belong to A'_1 and E' symmetries. The remaining modes, A''_2, 2E' and E'' are associated with the angle deformations. One of these, E', is related to the equatorial deformation and the rest belong to the axial deformations. The internal coordinates of $TaBr_5$ are defined in Figure 1. The average Ta−Br bond is taken as 245 ppm (Wells, 1975) while the axial and equatorial angles equal 90^o and 120^o, respectively. The symmetry coordinates used for the construction of both the G and F matrices for $TaBr_5$ with D_{3h} symmetry as well as their descriptions are given in Table 1. The normal coordinate analysis was based on a general quadratic force field utilizing no non−bonded interactions. Here, the potential energy is expressed in terms of harmonic force constants associated with the coordinates of the molecule i.e. bond distances and the angles between them. The computer calculations were performed using a version of the Snyder−Schachtschneider programs (Schachtschneider, 1964). The value of the force constants are decided with the method described in previous communications (Nour, 1986; Nour *et al,* 1984 and 1986. The final set of both the diagonal and off-diagonal constants which give the best agreement between the observed and calculated frequencies are shown in Table 2.

The vibrations of a molecule may be described in terms of normal coordinates, Q_e, which are related to the symmetry coordinates, S_k, by the linear transformation (Califano, 1976):

$$S_k = \Sigma_e L_{ke} Q_e$$

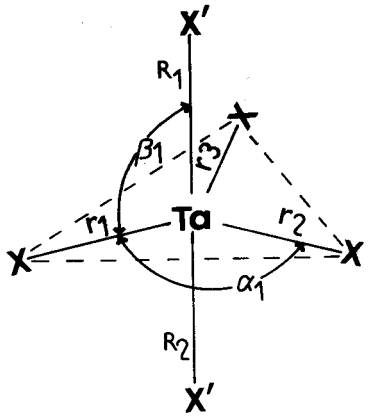

Fig. 1 : Internal coordinates for TaX_5.

where L_k are the normalized amplitude of vibrations. For a vibaration of frequency ν associated with the normal coordinates, Q_a, the potential energy of the molecule is given by:

$$2V = Q_a \Sigma_{ij} F_{ij} L_{ia} L_{ja}$$

such terms are large only when i = j, where the diagonal force constants, F_{ii}, are such greater than the off diagonal ones, Fij. Accordingly, the term $^1/_2 F_{ii} L^2_{ia}$ represents the distribution of the potential energy among symmetry coordinates, therefore, the obtained values of the potential energy distribution are of high assistance in deciding the correct assignments for each vibrational band as given in Table 3. for $TaBr_5$.

Two vibrational studies on $TaBr_5$ are known in the literature. The first study (Walton and Bridson, 1967) reported the infrared of the solid compound in Nujol mull and number of bands were mistakenly assigned to $TaBr_5$ monomer. As mentioned earlier in the text the species occurs in the solid state in the dimeric form, Ta_2Br_{10}. The other study (Beattie and Ozin, 1969) dealt with the Raman spectrum of the monomer in the gas phase and these data were imployed in our calculations. In their work, the $2A''_2$ mode (ν_3 and ν_4) were not reported because of their Raman inactivities and the E'(ν_5) mode also was missing.

The absence of these three modes caused some difficulties in performing complete analysis for the species. For this reason, two calculations with two sets of force constants were undertaken for $TaBr_5$. These were based on comparison with the frequency ordering of related species such as $NbBr_5$ and $TaCl_5$. In

calculation I, the analysis was performed in order to calculate the three missing modes (ν_3, ν_4 and ν_5) with similar ordering of frequencies to that of $NbBr_5$ ($\nu_5 > \nu_3 > \nu_1 > \nu_2 > \nu_6 > \nu_8 > \nu_4 > \nu_7$) (Nour, 1986). The calculation II produced similar ordering of frequencies to that of $TaCl_5$ ($\nu_5 > \nu_1 > \nu_3 > \nu_2 > \nu_6 > \nu_4 > \nu_8 > \nu_7$). It should be mentioned that in both calculations (I and II) the assignments of the other observed 5 bands (ν_1, ν_2, ν_6, ν_7 and ν_8) were kept unchanged. However, in both calculations the equatorial Ta−Br is much stronger (~ 1.65 times) than that of the axial Ta−Br bond. This is in agreement with our previous studies on related species (Nour, 1986) as well as with the M.O. treatment of MX_5 molecules (Rossi and Hoffmann, 1975) which concluded that the axial bonds should be weaker in the case of species with D_{3h} symmetry and d^0 structure as in $TaBr_5$. The values of the diagonal force constants of calculation I are higher than those of calculation II. The opposite is observed for the interaction (off diagonal) constants, Table 2. The low interaction constant values may favour calculation I and this suggests values of 165 and 261 Nm^{-1} for the Ta−Br (axial) and Ta−Br (equatorial) bonds, respectively, and that the frequency values of ν_3 ; A″2, ν_4 ; A″2 and ν_5 ; E′ are calculated at 263, 89 and 308 cm^{-1}, respectively. Calculation I was also favoured by its frequency ordering similarity to $NbBr_5$, Table 4. The value of the potential energy distribution shown in Table 3. indicate, as expected, the coupling between the motions of the same symmetry blocks and this is more pronounced in the case of the three E′ modes. Such coupling is limited in the case of the $2A'_1$ modes, since the motion of the central T_a atom in these modes is expected to be very small.

Comparing both the assignments and the force constant values for $TaBr_5$ with those previously reported (Nour , 1986) for $NbBr_5$, (Tables 4 and 5) it seems that the difference between the values of the two compounds is too small and does not reflect the differnce in atomic numbers between the two atoms (Nb; 41e and Ta; 71e). This may be explained by the fact that the ionic size of both ions are almost the same (ionic radius for Nb^{5+} and Ta^{5+} are 0.7 And 0.73 A, respectively) and this agrees with the fact that the average metal−bromide bond lengths in both $TaBr_5$ and $NbBr_5$ are very close . These are 245 and 246 ppm, respectively.

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Table 1

Symmetry coordinates and their descriptions for $TaBr_5$.

A_1' :	$S_1 = \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3)$		; Ta–Br stretch
	$S_2 = \frac{1}{\sqrt{2}}(R_1 + R_2)$		; Ta–Br′ stretch
	$S_3 = \frac{1}{\sqrt{3}}(\alpha_1 + \alpha_2 + \alpha_3)$		; redundant
	$S_4 = \frac{1}{\sqrt{6}}(\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6)$		; redundant
A_2'':	$S_5 = \frac{1}{\sqrt{2}}(R_1 - R_2)$		; Ta–Br′ stretch
	$S_6 = \frac{1}{\sqrt{6}}(\beta_1 + \beta_2 + \beta_3 - \beta_4 - \beta_5 - \beta_6)$		; Br–Ta–Br′ bend
E' :	$S_7 = \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)$	}	; Ta– Br stretch
	$S_8 = \frac{1}{\sqrt{2}}(r_2 + r_3)$	}	
	$S_9 = \frac{1}{\sqrt{6}}(2\alpha_1 - \alpha_2 - \alpha_3)$	}	; Br–Ta–Br bend
	$S_{10} = \frac{1}{\sqrt{2}}(\alpha_2 - \alpha_3)$	}	
	$S_{11} = \frac{1}{\sqrt{12}}(2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6)$	}	; Br–Ta–Br′ bend
	$S_{12} = \frac{1}{2}(\beta_2 - \beta_3 + \beta_5 - \beta_6)$	}	
E''	$S_{13} = \frac{1}{\sqrt{12}}(2\beta_1 - \beta_2 - \beta_3 - 2\beta_4 + \beta_5 - \beta_6)$	}	; Br–Ta–Br′ bend
	$S_{14} = \frac{1}{2}(\beta_2 - \beta_3 - \beta_5 + \beta_6)$	}	

Table 2

Force constants * for $TaBr_5$

Symbol	Description	Value		Symbol	Description	Value	
		Cal. I	Cal. II			Cal. I	Cal. II
F_R	Ta–X′	165	136	F_{Rr}	Ta–X′, Ta–X	7	8
F_r	Ta–X	261	231	F_{rr}	Ta–X, Ta–X	4	13
F_β	X–Ta–X′	81	81	$F_{\alpha\alpha}$	X–Ta–X, X–Ta–X	5	—
F_α	X–Ta–X	68	72	$F_{\beta\beta}$	X–Ta–X′, X–Ta–X′	—	4
F_{RR}	Ta–X′, Ta–X′	—	18				

* Stretching constants in Nm^{-1}, bending constants in Nm^{-1} Rad^2.

Table 3

Observed and calculated frequencies (cm^{-1}), potential energy ditributions (P.E.D.) and qualitative assignments for $TaBr_5$.

Calculation	Frequency		P.E.D. *				Assignments
	Obs.	Calc.	F_R	F_r	F_α	F_β	
Cal. I:	240	240	2	98	0	0	A_1': ν(Ta−Br)
	182	186	96	4	0	0	ν(Ta−Br')
	—	263	95	0	0	5	A_2'': ν(Ta−Br')
	—	89	6	0	0	94	δ(BrTaBr')
	—	308	0	95	3	2	E': ν(Ta−Br)
	110	108	0	4	86	10	δ(BrTaBr)
	70	68	0	1	12	87	δ(BrTaBr')
	93	92	0	0	0	100	E": δ(BrTaBr')
Cal. II:	240	235	2	98	0	0	A_1': ν(Ta−Br)
	182	179	95	5	0	0	ν(Ta−Br')
	—	226	92	0	0	8	A_2'': ν(Ta−Br')
	—	92	11	0	0	89	δ(BrTaBr')
	—	285	0	94	4	2	E': ν(Ta−Br)
	110	111	0	6	85	9	δ(BrTaBr)
	70	70	0	1	11	88	δ(BrTaBr')
	93	90	0	0	0	100	E": δ(BrTaBr')

* Normalized to total 100 for the diagonal force constant distributions.

Table 4

Vibrational assignments for $TaBr_5$ and $NbBr_5$.

$TaBr_5$	$NbBr_5$*	Assignments	$TaBr_5$	$NbBr_5$*	Assignments
240	234	$\nu_1(A_1')$	308	315	$\nu_5(E')$
182	178	$\nu_2(A_1')$	110	119	$\nu_6(E')$
263	288	$\nu_3(A''_2)$	70	67	$\nu_7(E')$
89	93	$\nu_4(A_2'')$	93	101	$\nu_8(E'')$

* (Nour, 1986)

Table 5

Force constants for $TaBr_5$ and $NbBr_5$.

Symbol	$TaBr_5$	$NbBr_5$*	Symbol	$TaBr_5$	$NbBr_5$*
F_R	165	142	F_{Rr}	7	7
F_r	261	217	F_{rr}	4	15
F_α	81	92	$F_{\alpha\alpha}$	5	—
F_β	68	94	$F_{\beta\beta}$	—	−4
E_{RR}	—	5	$F_{r\beta}$	—	14

(Nour, 1986)

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التحليل الترددي للمتراكب $Ta\,Br_5$

المتولي السيد نور

يُعني هذا البحث بحسابات نظرية المجموعة ، group theory ، وكذلك تعيين ثوابت القوى ، force constants ، للمتراكب $TaBr_5$ باستخدام الحاسب الآلي . وقد أجريت الحسابات للمتراكب تحت نقطة تماثل من نوع D_{3h} حيث أمكن تحديد قيم جميع الترددات وعددها ١٢ حركة ترددية : $2A_1' + 2A_2'' + 3E' + E''$

وتوضح قيم ثوابت القوى للروابط المحورية، Ta–Br' ، والاستوائية ، Ta–Br ، وهي ١٦٥ و ٢٦١ نيوتن م–١ على التوالي ان الرابطة الاستوائية أقوى من الرابطة المحورية بمقدار ١,٦٥ مرة وقد فسرت هذه النتائج في ضوء طبيعة هذه الروابط .

تضمنت هذه الدراسة أيضا تعيين قيم الترددات من نوع : ν_3, ν_4, ν_5 والتي لم تظهر في القياسات المعملية وذلك عند قيم ٢٦٣ ، ٨٩ ، ٣٠ سم–١ على التوالي .