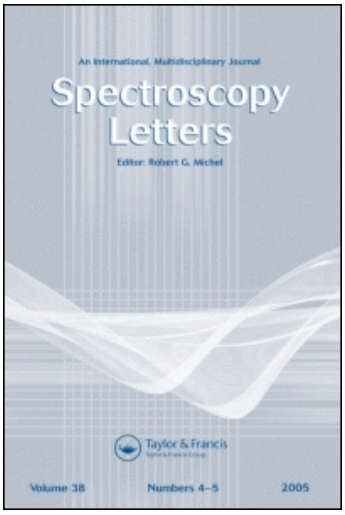

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Spectroscopically Active Frequencies of $PMo_{12}O_{40}^{3-}$

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SPECTROSCOPICALLY ACTIVE FREQUENCIES OF $PMo_{12}O_{40}^{3-}$

Keywords: Molecular vibrations, Force constants, Vibrational frequencies, $PMo_{12}O_{40}^{3-}$

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ABSTRACT

A 53-atomic model of T_d symmetry was assumed for the $PMo_{12}O_{40}^{3-}$ ion. It was succeeded to perform a complete vibrational analysis for this structure. The main force constants are reported along with the complete sets of spectroscopically active frequencies, viz.: $9A_1$(Ra) + 13E (Ra) + $22F_2$(ir+Ra). The calculated values are tentatively correlated with infrared data from literature and so far unpublished Raman data.

A detailed vibrational analysis of the $PMo_{12}O_{40}^{3-}$ ion was initiated simultaneously with a new Raman investigation[1] of compounds with Keggin structures.[2] This analysis is preceded by other vibrational studies of cage structures.[3-6] In Keggin structures a multitude of cages can be distinguished, and a complete vibrational analysis of such a complex

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and relatively large structure (53 atoms) represented a challenging problem. It was not unexpected that features encountered in the previous analyses[3-5] of cage structures were enhanced in the present case.

MOLECULAR MODEL

The $PMo_{12}O_{40}^{3-}$ ion was treated in terms of a 53-atomic model of T_d symmetry. This is an idealized structure deduced from x-ray data.[7] A P atom is surrounded tetrahedrally by four O atoms here referred to as O(P). Each O(P) forms the apex in a trigonal Mo_3O_7 structure; cf. Fig. 1(a). In each of these structures there are three terminal oxygen atoms, O_t. The Mo atoms take part in a puckered Mo_3O_3 ring and nearly planar MoOMoO(P) rings. The four Mo_3O_7 parts are linked together by oxygen bridges (O_b), which together with the Mo atoms form Mo_3O_3 rings of another type. Octahedral coordination of O atoms around each Mo is completed when adding six O_b atoms to each Mo_3O_7 structure. Thus the trigonal Mo_3O_{13} structure emerges; cf. Fig. 1(b).

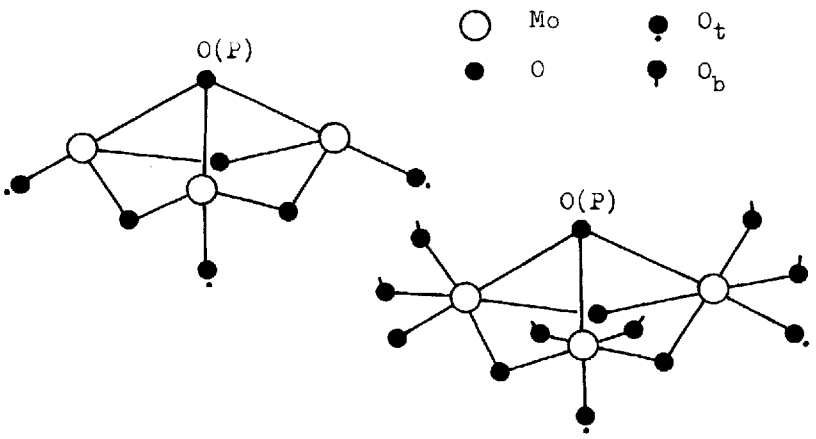

FIG. 1. Trigonal fragments of the $PMo_{12}O_{40}$ structure: (a) Mo_3O_7, (b) Mo_3O_{13}.

MOLECULAR VIBRATIONS

The normal modes of vibration are distributed among the species of the symmetry group T_d according to

$$\Gamma_{vib} = 9A_1 + 4A_2 + 13E + 16F_1 + 22F_2$$

Symmetry coordinates were constructed by the method of classification of the vibrational modes into (a) framework vibrations, (b) framework-ligand couplings, (c) ligand vibrations, and (d) interligand vibrations. The theory and systems of general equations developed for tetrahedral complexes with trigonal ligands[8,9] were employed. In this connection the Mo_3O_7 groups were considered as ligands. The procedure was found useful although the ligand concept in the present case is based on a mathematical viewpoint rather than a chemical one.

PRINCIPLES OF CALCULATION

A diagonal force field in terms of valence coordinates including redundancies was assumed. The valence coordinates are: (a) all stretchings, (b) all bendings, but excluding the nearly linear bendings for opposite bonds in the octahedra around each Mo, and finally (c) selected PO torsions and all MoO torsions in six-membered and four-membered rings. The total number of valence coordinates is 382; hence 223 redundancies are present. The most important force constant values are those of the stretchings: 4.5 for P-O, 0.8 for Mo-O(P), 7.4 for Mo-O_t, and 4.0 for all other Mo-O bonds; all values in mdyne/Å. For the different bendings values from 0.25 to 0.45 mdyne/Å were taken, and all torsional force constants were assumed to be 0.01 mdyne/Å.

The diagonal force constant matrix was converted to F matrix blocks in terms of symmetry coordinates, and the corresponding vibrational frequencies were computed.

TABLE 1

Calculated and Observed Frequencies for $PMo_{12}O_{40}^{3-}$

Calculated A_1	Calculated E	Calculated F_2	Tentative description	Observed ir	Observed Raman
		1107	P-O stretch	1070	1090 (vw)
980			P-O stretch	990[a]	996 (vs)
	973	974	Mo-O_t stretch	965	
959		969	Mo-O_t stretch		977 (s)
	945	941	Mo-O(P) stretch	898[a]	895
	883	885		870	825 (?)
	762	800	Mo-O_b stretch	790	
687		687	Mo-O(P) stretch		718
	674	677			710
582					602 (s)
		571		598	
	547	547		560[a]	580[b]
502		485		500	495 (w)
		469		456[a]	463
450	441	447		460	463
		412	bridge stretchings and deformations	410	406[b]
		358		380	370(doublet)
		327		340	340 (?)
301	315				missing(?)
	295				
		283		282	
		266		265	
239	246				247 (s)
		232		220	220
		216		220	220 (broad)
202	201				200
		194		-	157(doublet)
	174	169		-	157
	153				110(doublet)
					75

[a] From Lange et al.[10]; all other infrared frequencies from Thouvenot et al.[11]

[b] From Thouvenot et al.[11]; all other Raman frequencies from Lyhamn et al.[1]

RESULTS AND DISCUSSION

The theory predicts $9A_1 + 13E + 22F_2$ fundamentals active in Raman, while those of species F_2 also should be active in infrared. The $4A_2 + 16F_1$ fundamentals are inactive. All the spectroscopically active frequencies calculated from the present force field (see above) are collected in Table 1. They are tentatively correlated with experimental data available so far.[1,10,11] The table also includes a suggestion to a partial approximate description of the normal modes.

It is clear that the present approximate analysis cannot predict the fundamental frequencies with any large degree of accuracy. Nevertheless we find the calculated frequencies to be distributed in the same ranges as the experimental frequencies and also several instances of quantitative agreements.

Details of the present work are to be published elsewhere.[12]

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