

Normal Coordinate Analysis of MoF₅ & MoCl₅

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The vibrational spectra of MoF₅ and MoCl₅ have been interpreted in terms of the normal coordinate treatment based on D_{3h} symmetry of the molecules employing a valence force field. The good fit between the observed and calculated frequencies as well as the potential energy distribution values has made it possible to assign all vibrations. Force constant values indicate the weakness of the axial Mo-X' bonds compared with the equatorial Mo-X bonds for both the molecules. The effect of change in the coordinated halide from F⁻ to Cl⁻ in term of the force constant values of MoF₅ and MoCl₅ is discussed.

The assignments of the vibrational spectra of some monomeric pentahalide metal complexes (MX₅), is still a matter of dispute. Acquista and Abramowitz¹ studied the infrared spectrum of NbF₅ and concluded that this species belongs to the square pyramidal structures (C_{4v} symmetry), while some other workers^{2,3} assigned the spectrum on the basis of the trigonal bipyramidal (D_{3h}) structure. X-ray studies on MoF₅ single crystal^{4,5} indicated that the species crystallizes to form square tetramers in which the four Mo atoms are joined through fluorine bridges and that it is isostructural with NbF₅. However, Acquista and Abramowitz⁶ reported on the basis of their infrared matrix isolation study that the MoF₅ monomer has the D_{3h} symmetry. The same conclusion was also drawn by some other workers^{7,8}. Despite the fact that these studies agree on the D_{3h} symmetry for the MoF₅ monomer, there are wide differences in their reported band assignments. Similar D_{3h} symmetry was reported for the analogous MoCl₅ monomer on the basis of the gas-phase Raman study by Beattie and Ozin⁹. The crystal structure of MoCl₅ is reported¹⁰ to consist of dimers with chlorine atoms forming two octahedra which share a common edge.

The pentachlorides of phosphorous, antimony and niobium have been shown to have the D_{3h} symmetry^{11,12} as well as the pentafluorides of antimony, phosphorous, vanadium and arsenic¹¹⁻¹⁴. However, other species such as SF₅⁻, SeF₅⁻ and TeF₅⁻ belong to the C_{4v} symmetry¹⁴. The bonding and structures for both the D_{3h} and C_{4v} models are discussed by Rossi and Hoffmann¹⁵. Normal coordinate analyses have been reported for some

pentahalide complexes^{11,14,16,17}, but no such analysis is reported for MoF₅ and MoCl₅.

The main aim of this study is to present the normal coordinate analysis for MoF₅ and MoCl₅ molecules in order to make a full assignments of vibrational modes for each molecule based on the calculated potential energy distribution values and to clarify the ambiguity regarding the assignments, particularly for MoF₅.

Method of Calculation

The eight fundamental vibrations associated with each of the pentahalide molybdenum complex are distributed over the D_{3h} symmetry species $2A'_1 + 2A'_2 + 3E' + E''$.

The normal coordinate analysis was carried out for both MoF₅ and MoCl₅ using the GF matrix method based on a general quadratic force field utilizing no non-bonded interactions. The internal coordinates in these compounds are shown in Fig.1. The symmetry coordinates for the 12 vibrations were constructed as previously explained^{11,16}. The average Mo-F and Mo-Cl bond lengths were taken equal to 185 and 224

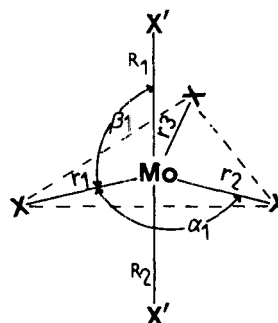


Fig. 1—Definition of internal coordinates in MoX₅ (X = Cl or F)

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ppm, respectively^{5,10}. The computer calculations were done using modified versions of the programs of Schachtschneider¹⁹. The initial force constants were introduced and perturbed until the best fit between the observed and calculated frequencies was obtained; then the off-diagonal constants were added one by one to improve the calculations. Finally, the diagonal and off-diagonal elements were refined simultaneously to obtain the best set of force constants as a whole for both MoF₅ and MoCl₅ as shown in Table 1. The observed and calculated frequencies and their assignments based on the calculated potential energy distribution values are given in Table 2.

Results and Discussion

Interestingly, the trends in the distribution values in both MoF₅ and MoCl₅ are similar and lead to quantitative assignments for each compound. Moreover, the assignments show almost the same order of frequencies for both compounds. Similar order was also observed in our previous studies on NbCl₅ and NbBr₅¹⁶. Our assignments, for MoCl₅ (Table 2) agree with those reported by Beattie and Ozin⁹ based on their gas-phase Raman study. The two bands associated with A₂' species related to ν₃ and ν₄, which are Raman-inactive, are calculated to be at 401 and 149 cm⁻¹, respectively. On the other hand, our assignments for MoF₅ (Table 2) agree with those reported by Acquista and Abramowitz⁶ based on their infrared matrix study, and disagree with the assignments reported by Bates⁷ and by Quellette *et al.*⁸. Such disagreement could arise from mistaken assignment of some bands of the tetramers to the MoF₅ monomer by Bates⁷ and Quellette *et al.*⁸. It should be noted that the solid MoF₅ consists mainly of the tetramer^{4,5} and hence the Raman spectra of the solid reported by Bates⁷ should not be associated with the monomer. In the liquid phase, it seems that both the monomer and tetramer of MoF₅ co-exist. The spectra of the liquid reported by Quellette *et al.*⁸ show that beside the bands of the monomer, there are a number of bands at 747, 500 and 440 cm⁻¹ which should

Table 1—Force Constants* for MoF₅ and MoCl₅

Symbol	Description	Value*	
		MoF ₅	MoCl ₅
f_R	Mo-X'	391.0	196.0
f_i	Mo-X	485.0	258.0
f_a	X-Mo-X	51.4	81.1
f_β	X-Mo-X'	41.0	79.3
$f_{a\beta}$	X-Mo-X, X-Mo-X'	12.2	12.5
f_{RR}	Mo-X', Mo-X'	15.0	12.0
f_{Rr}	Mo-X', Mo-X	3.0	8.0
f_{rr}	Mo-X, Mo-X	29.4	21.0
$f_{\beta\beta}$	X-Mo-X', X-Mo-X'	—	-4.0
$f_{r\beta}$	Mo-X, X-Mo-X'	19.3	16.2

*Stretching constants in Nm⁻¹, bending constants in Nm⁻¹ Rad²

Table 2—Observed and Calculated Frequencies (cm⁻¹), Potential Energy Distribution (PED) and Vibrational Assignments for MoF₅ and MoCl₅

Compound	Frequency		PED†				Assignments
	Obs.†	Calc.	f_R	f_i	f_a	f_β	
MoF ₅	703	699	1	99	0	0	A ₁ : ν(Mo-F)
	—	602	99	1	0	0	ν(Mo-F)
	683	686	98	0	0	2	A ₂ ': ν(Mo-F)
	—	181	1	0	0	99	δ(FMoF)
	713	719	0	97	2	1	E*: ν(Mo-F)
	261	259	0	1	87	12	δ(FMoF)
	112	115	0	3	28	69	δ(FMoF)
	201	201	0	0	0	100	E'': δ(FMoF)
MoCl ₅	390	387	5	95	0	0	A ₁ : ν(Mo-Cl)
	313	311	93	7	0	0	ν(Mo-Cl)
	—	401	94	0	0	6	A ₂ ': ν(Mo-Cl)
	—	149	6	0	0	94	δ(ClMoCl')
	418	421	0	94	4	2	E*: νMo-Cl
	200	198	0	5	77	18	δ(ClMoCl)
	100	104	0	2	27	71	δ(ClMoCl')
	175	173	0	0	0	100	E'': δ(ClMoCl')

*Coupled motions

†Observed values for MoF₅ are taken from refs 6 and 8 and for MoCl₅ from ref.9.

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

be associated with the tetramer. This was judged by comparing the liquid spectrum reported by Quелlette *et al.*⁸ with the solid tetramer spectrum of Bates⁷. However, the monomer may be generated in higher ratio in the gas phase as in the case of MoCl₅ (ref. 9), or may be isolated in a low temperature matrix as in MoF₅ (ref. 6). The two bands reported by Quелlette *et al.*⁸ at 703 and 201 cm⁻¹ and assigned by them to $\nu_2(A_1')$ and $\nu_7(E')$ modes, respectively, should be on the basis of our work assigned to $\nu_1(A_1')$ and $\nu_8(E'')$ modes, respectively. The latter two modes are infrared-inactive and, therefore, were not reported in the matrix spectrum of Acquista and Abramowitz⁶.

Table 1 shows that the axial Mo-F' and Mo-Cl' bond stretching force constants (f_R) are 391 and 196 Nm⁻¹, respectively. The corresponding values for the equatorial Mo-F and Mo-Cl bonds (f_r) are 485 and 258 Nm⁻¹. Since the force constant value is an approximate measure of the relative bond strength, the above f_R and f_r values indicate that the bonds in MoF₅ are much stronger compared with those of MoCl₅, as also expected from the smaller size of F⁻. Secondly, the equatorial Mo-X bonds are 1.24 and 1.32 times stronger than the axial Mo-X' bonds in MoF₅ and MoCl₅, respectively. In general, these values may indicate a higher covalent character for the equatorial bonds since force constant value reflects only the covalent properties of the bond. This conclusion agrees with that derived from the M.O. treatment of the pentacoordinate species^{15,20}.

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