

VIBRATIONAL SPECTRA AND NORMAL COORDINATE TREATMENT OF MOLYBDENUM TRIOXIDE

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This paper presents the near infrared spectrum and Fourier far infrared spectrum of molybdenum trioxide from $625-4000\text{ cm}^{-1}$ and $100-650\text{ cm}^{-1}$ respectively. The vibrational analysis is made on the basis of C_{3v} symmetry and general quadratic valence force constants are determined. The fundamental frequencies of MoO_3 are: $A_1 = 850, 350\text{ cm}^{-1}$; $E = 1000, 373\text{ cm}^{-1}$. Further using the values of the present potential constants, other molecular constants are also evaluated. The thermodynamic properties are presented over the temperature range 298.16 K to 1000 K.

Keywords : Vibrational Spectra; Molybdenum Trioxide; Infrared Spectrum; Thermodynamic Properties

INTRODUCTION

MOLYBDENUM oxide has several important industrial applications at relatively high temperatures as catalysts and thus the structural and spectroscopic data are of great value. Structure of known trioxides, which have hitherto been investigated^{1,2} fall into two categories, those having D_{3h} symmetry such as SO_3 and others having C_{3v} symmetry such as WO_3 . In the course of our investigation on the study of molecular constants of pyramidal type molecules our attention has turned to molybdenum trioxide.

Nagarajan³ carried out the normal coordinate analysis of MoO_3 using the estimated frequencies for a D_{3h} symmetry. The vibrational frequencies of this molecule has been given by Hewett *et al.*⁴ on the basis of C_{3v} symmetry. According to Hewett *et al.*⁴, the symmetric stretch ($Mo-O$) frequency is higher than the asymmetric stretch frequency. But later studies revealed that the asymmetric frequency is much more intense than the symmetric frequency for slightly non-planar molecules⁵⁻⁷. On this basis we assigned higher value for the asymmetric frequency in the present study. Further¹ proposed the bending frequencies viz., $\nu_2(A_1)$ and $\nu_4(E)$ from the combination band.

The present study was initiated to obtain the complete vibrational frequencies of MoO_3 and to determine whether a C_{3v} configuration may be adopted to explain vibration of MoO_3 in agreement with normal coordinate analysis.

EXPERIMENTAL

Molybdenum trioxide was obtained from Fluka A.G., Chemische Fabrick, Schweiz. The infrared spectra of MoO_3 have been recorded on Perkin Elmer IR-257 double

beam grating spectrophotometer in the region 625 to 4000 cm^{-1} . The Fourier transform IR spectra has also been recorded on polytec FIR-30 in the region 100–650 cm^{-1} , and the observed frequencies are listed in Table I. The frequencies for all sharp bands are expected to be accurate to $\pm 1 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Four fundamental absorption bands have been observed at 1000, 850, 375 and 350 cm^{-1} . The band at 1000 cm^{-1} is very much stronger than that at 850 cm^{-1} . The observed frequencies along with their assignments are given in Table I.

The vibrational representation of a XY_3 planar (D_{3h}) molecule is represented as $\Gamma = A_1 + A_2' + 2E'$, whereas that of a XY_3 pyramidal (C_{3v}) molecular as $\Gamma = 2A_1 + 2E$. Accordingly, in a planar molecule only three frequencies (A_2' and $2E'$) are infrared active, while in a pyramidal system all the four frequencies ($2A_1$ and $2E$) should be active in the infrared. In both the systems, the ν_1 and ν_4 stretching modes are expected to occur at frequencies higher than the ν_2 and ν_3 bending deformations. The appearance of two high frequency infrared bands at 1000 and 850 cm^{-1} suggests the C_{3v} molecular symmetry for this molecule, which is in consistency with those concluded by Hewett *et al.*⁴. The assignment of the high frequency fundamentals (stretching modes) can be made on the basis of their relative intensity. For slightly non-planar molecules, one expects the $\nu_3(E)$ mode to be much more intense than $\nu_1(A_1)$. On this basis we assign the band at 850 cm^{-1} to be $\nu_1(A_1)$ and that at 1000 cm^{-1} to be $\nu_3(E)$.

However the low frequency $\nu_2(A_1)$ and $\nu_4(E)$ bands are more difficult to assign, as no definite guidelines exist for intensity and relative magnitude of the frequencies.

TABLE I
Assignments of fundamental infrared frequencies (cm^{-1}) of Molybdenum trioxide

Region	Frequency (Intensity*)	Assignment
Infrared	850 (S)	ν_1 (Mo — O symmetric stretch)
	1000 (VS)	ν_3 (Mo — O asymmetric stretch)
	1150 (W)	$2\nu_3 - \nu_1$
	1305 (VW)	$2\nu_3 - 2\nu_2$
	1340 (W)	$2\nu_1 - \nu_3$
	1625 (W)	$2\nu_3 - \nu_4$
Fourier far	106 (VW)	$\nu_1 - 2\nu_4$
	147 (VW)	$\nu_1 - 2\nu_2$
infrared	280 (S)	$\nu_3 - 2\nu_2$
	350 (M)	ν_2 (O — Mo — O symmetric bending)
	373 (S)	ν_4 (O — Mo — O asymmetric bending)

*VS : Very Strong; M : Medium; VW : Very Weak; S : Strong; W : Weak;

It has been observed that in the case of pyramidal systems $\nu_2(A_1) < \nu_4(E)$. Hence, following the assignment of bending modes due to Wesley and Decock⁵⁻⁷, we have assigned $\nu_2(A_1)$ mode at 350 cm^{-1} and $\nu_4(E)$ to 373 cm^{-1} band. This is in agreement with the assignment $\nu_2(A_1)$ 300 cm^{-1} and $\nu_4(A_1)$ 350 cm^{-1} in case of WO_3 ⁸.

NORMAL COORDINATE ANALYSIS

A normal coordinate analysis of Molybdenum trioxide has been carried out following Wilson's F-G matrix method on the basis of C_{3v} point group, using a general quadratic potential function and molecular kinetic constants and a set of force constants have been reported.

The symmetry coordinate and the other details of the procedure are the same as those given in the earlier papers^{9,10}.

The kinetic constants, the force constants, the compliance constants and the mean square amplitudes of vibration at 298.16 K are given in Table I. As expected, the interaction force constants f_{dd} , $f_{\alpha\alpha}$ and $f_{d\alpha}$ assume negative sign for this type of molecule. Further, the same sign is noted for the kinetic constants and potential constants in the case of bond angle interaction. For the molecule under study, the bond-bond interaction force constant assumes a negative sign. This result is in line with the previous observation made with respect to the molecules having oxygen as the Y atom¹¹. The present set of force constants have been utilized in evaluating compliance constants, valence mean square amplitudes, coriolis coupling constants and centrifugal distortion constants.

The compliance constants are evaluated for this molecule by Decius method¹². These constants naturally show the trend opposite to that relating to the force constants. Using the force constants in Cyvin's secular equation¹³ the symmetrized mean square amplitude elements and hence the vibrational mean amplitudes have been obtained. From Table II, it may be seen that the mean amplitudes for the bonded

TABLE II
Values of kinetic constants (10^{-23} g); Force constants (10^5 dynes/cm), Compliance constants (m dyne/A) and Mean square amplitudes (Both bonded and nonbonded (10^{-3} \AA^2) at 298.16K)

Constants	d (Mo - O)	dd	α	$\alpha\alpha$	d α	d α'
Kinetic constants	2.3341	0.0647	0.2855	0.0123	- 0.0215	0.0825
Force constants	7.3454	- 0.5858	0.1349	- 0.0001	- 0.0135	0.0379
Compliance constants	0.1385	0.0121	1.8598	0.0015	0.0035	- 0.0206
Bonded mean square amplitudes	1.3237	0.0481	9.5691	- 0.0638	0.0525	- 0.1904
Non bonded mean square amplitudes	σ_q (0...0)	$\sigma_{\alpha\alpha}$	$\sigma_{d\alpha}$	$\sigma'_{d\alpha}$		
	5.2022	0.6960	0.9264	0.1074		

as well as the non-bonded distances obtained in the present investigation are in the characteristic range for $M_o - O$ vibration. As expected, $l_{0\dots0}$ is greater than l_{M_o-o} , which is contrary to the corresponding force constants. Thus, it is clear that in the metal oxides, mean vibrational amplitudes are characteristic to some extent. The present set of values will be useful in the interpretation of electron-diffraction data relating to this molecule. The present set of values for the vibrational mean amplitudes once again confirms the correctness of our assignment.

The first order Coriolis coupling constants of the $E \times E$ type as well as the second order constants of the type $A_1 \times E$ type have been evaluated by following the matrix relation, $\zeta^\alpha = L^{-1} C^\alpha(L^{-1})$, making use of kinetic constants. The $C^\alpha (\alpha = x, y, z)$ matrix elements have been obtained by the vector method of Meal and Polo^{14,15}. The Zeta values listed in Table IV obey the sum rules given by Oka¹⁶. These values further satisfy the relations :

$$\begin{aligned}
 &(\zeta_{1a3a}^y)^2 + (\zeta_{1a4a}^y)^2 + (\zeta_{2a3a}^y)^2 + (\zeta_{2a4a}^y)^2 + (\zeta_{3a4a}^y)^2 = 1 \\
 &2[(\zeta_{1a3a}^y)^2 + (\zeta_{1a4a}^y)^2 + (\zeta_{2a3a}^y)^2 + (\zeta_{2a4a}^y)^2 - \frac{1}{2}] \\
 &\quad - (\zeta_{3a4b}^z)^2 + (\zeta_{3a3b}^z)(\zeta_{4a4b}^z) = 0 \\
 &(\zeta_{1a3a}^y)(\zeta_{2a4a}^y) - (\zeta_{1a4a}^y)(\zeta_{2a3a}^y) = 0
 \end{aligned}$$

As expected, the values of ζ_{13}^y , ζ_{15}^y and ζ_{44}^z are negative. Further, the magnitude of ζ_{23}^y and ζ_{34}^z are of the same order. The high values of the constants ζ_{23}^y and ζ_{34}^z show that the coupling concerned is much stronger.

TABLE III
 Mean amplitudes ($10^{-3}A$) at 298.16 K; Coriolis coupling constants and centrifugal distortion constants (KHz)

Mean amplitudes	Coriolis coupling constants	Centrifugal distortion constants
	$\zeta_{3a3b}^z \quad \zeta_{3a4a}^y \quad \zeta_{1a4a}^y \quad \zeta_{2a4a}^y$	D_I
1 ($M_o - o$)	$\zeta_{4a4b}^z \quad \zeta_{1a3a}^y \quad \zeta_{2a3a}^y$	D_{JK}
1 ($0\dots0$)	ζ_{3a4b}^z	D_K
3.6383	0.1604 0.3708 - 0.0872 0.5242 4.5385	
7.2126	- 0.4353 - 0.1250 0.7514	- 6.3962
	0.8095	3.4436

The determination of the exact rotation energy levels of a non-rigid molecule requires the knowledge of centrifugal distortion constants. The centrifugal distortion constants of Molybdenum trioxide have been calculated by Kivelson and Wilson method^{17,18} using the force constants obtained in the present investigation. They are reported in Table III. As expected, the value of D_{JK} is negative for this molecule.

The thermodynamic functions for MoO_3 have been evaluated for the ideal gas state at 1 atm assuming a rigid rotor harmonic oscillator model. The influence of spin contribution, anharmonicity and non rigidity are neglected. The contribution to the vibrational part of these thermodynamic functions have been calculated from the tables given by Johnson *et al*¹⁹. The values are presented in Table IV. The constants are useful to interpret the experimental results on thermodynamic properties.

TABLE IV
Heat content, free energy, entropy and heat capacity (in cal deg⁻¹ mol⁻¹) of MoO_3 for the ideal gaseous state at 1 atmospheric pressure

T (K)	$(H_0 - E_0)/T$	$-(F_0 - E_0)/T$	C_p^0	S^0
298.16	10.4183	51.2280	13.9064	61.6463
400	11.4705	54.5093	15.5703	65.9798
500	12.4530	57.1167	16.6980	69.5697
600	13.2675	59.5352	17.4727	72.6740
700	13.8717	61.5407	18.0086	75.4124
800	14.4231	63.4477	18.3967	77.8708
900	14.8738	65.1521	18.6741	80.0259
1000	15.2706	66.7557	18.8854	82.0263

CONCLUSION

A complete vibrational analysis of MoO_3 using the vibrational frequencies obtained from infrared and Fourier far infrared spectra is available on the basis of C_{3v} symmetry in the present study.

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