

SHORT COMMUNICATIONS

LASER RAMAN SPECTRUM AND NORMAL COORDINATE ANALYSIS OF MOLYBDENUM TRIOXIDE

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LASER Raman spectrum of molybdenum trioxide molecule from 50–4000 cm^{-1} is presented here. The vibrational analysis is made on the basis of C_{3v} symmetry for this molecule and the results are briefly discussed.

Molybdenum trioxide has several important industrial applications at relatively high temperatures as catalysts and the structural and spectroscopic data are of great value. During our investigation on the molecular constants of pyramidal type molecules our attention was turned to molybdenum trioxide. Nagarajan¹ studied the normal coordinate analysis of MoO_3 using the estimated frequencies for a D_{3h} symmetry. The vibrational frequencies of this molecule have been given by Hewett *et al*² on the basis of C_{3v} symmetry. According to Hewett *et al* 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 molecules³⁻⁵. On this basis a higher value for the asymmetric frequency was assigned in the present study. Further Hewett *et al* proposed the bending frequencies, viz $\nu_2 (A_1)$ and $\nu_4 (E)$ from the combination bands. The present study has been undertaken to obtain the complete vibrational frequencies of MoO_3 based on laser Raman spectrum and to determine whether a C_{3v} configuration may be adopted to explain the vibration of MoO_3 in agreement with normal coordinate analysis.

Molybdenum trioxide was obtained from Fluka A. G. Chemische Fabrik, Schweiz. The laser Raman spectrum of MoO_3 was recorded in CARY model 82 grating spectro-photometer in the region 50–4000 cm^{-1} .

The observed frequencies along with assignments are given in table 1. The appearance of two high frequency infrared bands at 993 and 814 cm^{-1} suggests the C_{3v} molecular symmetry for this molecule, which agrees with the results of Hewett *et al*. The high

Table 1 Assignments of fundamental Raman frequencies (cm^{-1}) of molybdenum trioxide

Frequency	Intensity*	Assignment
98	VW	$2\nu_4 - 2\nu_2$
192	W	$\nu_3 - \nu_1$
218	VW	$2\nu_2 - \nu_4$
282	S	ν_2 (O-Mo-O symmetric bending)
335	M	ν_4 (O-Mo-O asymmetric bending)
363	VW	$2\nu_3 - 2\nu_1$
375	W	$2\nu_4 - \nu_2$
661	M	$\nu_3 - \nu_4$
814	VS	ν_1 (Mo-O symmetric stretch)
906	VW	$2\nu_2 + \nu_4$
962	VW	$2\nu_1 - 2\nu_4$
993	VS	ν_3 (Mo-O asymmetric stretch)

*VS: very strong; W: weak; S: strong; VW: very weak; M: medium.

frequency fundamentals (stretching modes) can be assigned 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 814 cm^{-1} to be $\nu_1 (A_1)$ and that at 993 cm^{-1} to be $\nu_3 (E)$. Following the assignment of bending modes³⁻⁵ we have assigned $\nu_2 (A_1)$ mode at 282 cm^{-1} and $\nu_4 (E)$ to 335 cm^{-1} bands. This agrees with the assignment $\nu_2 (A_1) = 300 \text{ cm}^{-1}$ and $\nu_4 (E) = 350 \text{ cm}^{-1}$ in the case⁶ of WO_3 .

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 function and molecular kinetic constants and a set of force constants have been reported. The force constants, vibrational mean amplitudes at 298.16 K, Coriolis coupling constants and centrifugal distortion constants are given in table 2. As expected, the interaction force constants f_{dd} , f_{aa} and f_{da} assume negative sign for this type of molecule. This result is in line with the previous observation made with respect to the molecules having oxygen as the Y atom⁷. Comparing the force constant⁶ of WO_3 ($f_d = 9.3238 \text{ m dyn/A}$) with MoO_3 ($f_d = \text{m dyn/A}$), it is clear that in these iso-structural molecules, stable bond is achieved in molecules with heavier central atoms. This fact is well supported by the magnitudes of the vibrational frequencies $\nu_1 (A_1)$ of $\text{WO}_3 = 1045 \text{ cm}^{-1}$

Table 2 Values of force constants (10^5 dynes/cm), mean amplitudes (10^{-2} Å) at 298.16 K, Coriolis coupling constants and rotational distortion constants (kHz)

Force constants		Mean amplitudes		Coriolis coupling constants			
$f_d(\text{Mo-O})$	7.0961	$l_d(\text{Mo-O})$	3.6800	ζ_{3a3b}^z	0.1604	ζ_{1a4a}^y	-0.0872
f_{dd}	-0.7209	$l_d(\text{O...O})$	7.9603	ζ_{4a4b}^z	-0.4353	ζ_{2a3a}^z	0.7514
f_a	0.1017	Rotational distortion constants		ζ_{3a4b}^z	0.8095	ζ_{2a4a}^z	0.5242
f_{aa}	-0.0071	D_J	5.0940	ζ_{3a4a}^z	0.3707		
f'_{aa}	-0.0141	D_{JK}	-7.8870	ζ_{1a3a}^y	-0.1250		
f'_{aa}	0.0273	D_K	4.8931				

and $\nu_1 (A_1)$ of $\text{MoO}_3 = 814 \text{ cm}^{-1}$. The present set of force constants has been utilized in evaluating compliance constants, vibrational mean square amplitudes, Coriolis coupling constants and centrifugal distortion constants. The mean amplitudes for the bonded as well as non-bonded distances obtained in the present investigation are in the characteristic range for Mo-O vibration. As expected $l_{\text{O...O}}$ is greater than $l_{\text{Mo-O}}$, which is contrary to the corresponding force constants. Thus, it is clear that in metal oxides, mean vibrational amplitudes are characteristic to some extent. The present set of values will be useful to interpret the 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 values of ζ_{13}^y , ζ_{14}^y and ζ_{44}^z are negative. Further, the magnitude of ζ_{23}^z and ζ_{34}^z is of the same order. The high values of the constants ζ_{23}^z and ζ_{34}^z show that the coupling concerned is much stronger. As expected, the value of the rotational distortion constants D_{JK} is negative for this molecule. The thermodynamic functions for MoO_3 molecule are presented in table 3.

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Table 3 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	10.7853	51.5772	14.2582	62.3621
400	11.8813	54.9041	15.8249	66.7858
500	12.7918	57.6721	16.8920	70.4639
600	13.5380	60.0636	17.6215	73.6016
700	14.1564	62.1895	18.1263	76.3470
800	14.6763	64.1121	18.4834	78.7984
900	15.1063	65.8506	18.7445	80.9569
1000	15.4874	67.4816	18.9436	82.9691

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AGE RELATED CHANGES IN CATECHOLAMINE BIOSYNTHETIC ENZYMES OF RAT TISSUES

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It was reported earlier that the biogenic monoamines increase progressively in different tissues of rat during postnatal development¹. Many neurophysiological processes, such as motor activity, thermoregulation, sleep and hormonal secretion do in fact deteriorate during ageing²⁻⁵. Since catecholamines are known to be involved in these processes it seems important to understand the ageing effects on regulation of