

## SHORT COMMUNICATIONS

### LASER RAMAN SPECTRUM OF TUNGSTIC OXIDE

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LASER Raman spectrum of tungstic oxide in the region 100–2000  $\text{cm}^{-1}$  has been recorded. The fundamental frequencies have been assigned from the spectrum on the basis of  $C_{3v}$  symmetry for this molecule. Further, based on the present assignment, a complete vibrational analysis has been carried out for this molecule and the results are briefly discussed.

As a catalyst, the tungstic oxide has many industrial applications at fairly high temperature and hence its structural and spectroscopic data are of scientific interest. Studies have already been made<sup>1,2</sup> on the structure of  $\text{WO}_3$ . Weltner *et al*<sup>3</sup> have recorded the infrared spectrum of  $\text{WO}_3$  in neon and argon matrices but they assumed the planar  $D_{3h}$  symmetry. Further studies on  $\text{WO}_3$  revealed that the asymmetric frequency is much more intense than symmetric frequency for slightly non-planar molecules<sup>4–6</sup> like  $\text{MoO}_3$ . Since  $\text{WO}_3$  is isoelectronic with  $\text{MoO}_3$ , the high frequency value has been assigned to the asymmetric frequency mode in the present investigation. Further, in the previous studies the bending frequencies  $\nu_2(A_1)$  and  $\nu_4(E)$  have been predicted from the combination bands and not assigned. But in the present work, these frequencies have been assigned from laser Raman spectrum and a complete vibrational analysis has been carried out to check the correctness of the assignment.

Spectroscopically pure tungstic oxide has been obtained from Johnson and Mathiesson Company, England. The laser Raman spectrum of tungstic oxide has been recorded using 4880 Å line of  $\text{Ar}^+$  for excitation in the region 100–2000  $\text{cm}^{-1}$  at IIT (Madras) on Cary Model 82, grating spectrophotometer and a 4W argon laser.

The observed frequencies along with the assignment are presented in table 1. The appearance of two strong bands at 799 and 718  $\text{cm}^{-1}$  suggests the  $C_{3v}$  molecular symmetry for this molecule which agrees with the assignment proposed for  $\text{MoO}_3$  by Hewett *et al*<sup>7</sup>.

Table 1 Assignments of fundamental Raman frequencies ( $\text{cm}^{-1}$ ) of tungstic oxide

Frequency	Intensity*	Assignment
135	M	$\nu_1 - 2\nu_2$
240	W	$\nu_3 - 2\nu_2$
274	M	$2\nu_2 - \nu_4$
294	VW	$\nu_2(A_1)$ (O–W–O) symmetric bending)
324	M	$\nu_4(E)$ (O–W–O) asymmetric bending)
349	VW	$2\nu_4 - \nu_2$
415	VW	$\nu_1 - \nu_4$
434	VW	$\nu_1 - \nu_2$
580	VW	$2\nu_2$
618	VW	$\nu_2 + \nu_4$
638	VW	$2\nu_4$
718	VS	$\nu_1(A_1)$ (W–O symmetric bending)
799	VS	$\nu_3(E)$ (W–O asymmetric bending)

\* VS: Very strong; W: Weak; S: Strong; VW: Very weak; M: Medium.

Based on the relative intensity, the high frequency fundamentals (stretching modes) can be assigned. Also for slightly non-planar molecules, one expects the asymmetric mode  $\nu_3(E)$  to be much more intense than the symmetric mode  $\nu_1(A)$ . Based on these facts, we have assigned 718  $\text{cm}^{-1}$  as  $\nu_1(A)$  and 799  $\text{cm}^{-1}$  as  $\nu_3(E)$ . According to Wesley and Dekock<sup>4</sup>, in non-planar molecules, the bending modes  $\nu_2(A_1) < \nu_4(E)$ . Hence we have assigned 294  $\text{cm}^{-1}$  as  $\nu_2(A)$  and 324  $\text{cm}^{-1}$  as  $\nu_4(E)$ .

Using Wilson's F–G matrix method, the normal coordinate analysis of tungstic oxide has been carried out on the basis of  $C_{3v}$  point group. The symmetry coordinates and the other details of the procedure are the same as those given in the earlier papers<sup>8,9</sup>. The evaluated force constants, vibrational mean amplitudes at 298.16°K, Coriolis coupling constants and centrifugal distortion constants are reported in table 2. As expected the interaction force constants  $f_{dd}$ ,  $f_{aa}$ ,  $f_{da}$  assume negative sign. This result is in agreement with the previous observation made with respect to the molecules having oxygen as Y atom<sup>10</sup>. Comparing the value of force constant of  $\text{WO}_3$  ( $f_d = 5.1772 \times 10^5$  dynes/cm) with that of  $\text{MoO}_3$  ( $f_d = 7.46 \times 10^5$  dynes/cm) given by Hewett *et al*<sup>7</sup>, it may be seen that

**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			
$f_d(\text{W-O})$	5.1772	$l_d(\text{W-O})$	3.9545	$\zeta_{3a, 3b}^z$	0.0919	$\zeta_{1a, 3a}^y$	-0.0713
$f_{da}$	-0.2906	$l_{q(0 \dots 0)}$	8.0309	$\zeta_{4a, 3b}^z$	-0.4065	$\zeta_{1a, 4a}^y$	-0.0419
$f_\alpha$	0.1064	Rotational distortion constants		$\zeta_{3a, 4b}^z$	0.8050	$\zeta_{2a, 3a}^y$	0.7354
$f_{aa}$	-0.0001	$D_J$	0.1128	$\zeta_{3a, 4a}^y$	0.3966	$\zeta_{2a, 4a}^y$	0.4324
$f'_{da}$	-0.0078	$D_{JK}$	-0.1860				
$f'_{da}$	0.0152	$D_K$	0.2396				

the decrease of electronegativity of central atom, values at 298.16°K, Coriolis coupling constants and the value of stretching force constant obtained for  $\text{WO}_3$  is reasonable and has been well supported by the magnitude of vibrational frequencies  $\nu_1(A_1)$  of  $\text{WO}_3 = 718 \text{ cm}^{-1}$  and  $\nu_1(A_1)$  of  $\text{MoO}_3 = 814 \text{ cm}^{-1}$ . The present set of evaluated force constants have been used in the evaluation of other molecular constants. Further it may be seen that the mean amplitudes of vibration for the bonded as well as non-bonded distances obtained in the present work are in characteristic range of W-O vibration. As expected  $l_{0 \dots 0}(\sigma_q)$  is greater than  $l_{\text{W-O}}(\sigma_d)$ , which is contrary to the corresponding force constants. On comparing the bonded and non-bonded mean amplitudes of metal oxides such as  $\text{WO}_3$  and  $\text{MoO}_3$  given by Mohan *et al*<sup>11</sup> ( $l_{\text{W-O}} = 0.0395$ ,  $l_{0 \dots 0} = 0.0803$  and  $l_{\text{Mo-O}} = 0.0365$ ,  $l_{0 \dots 0} = 0.0796$ ), it is clear that the mean 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. Thus the values of the mean amplitudes of vibration evaluated in the present work confirm the correctness of the present assignment and hence the point group. In the evaluated zeta values,  $\zeta_{13}^y$ ,  $\zeta_{14}^y$ ,  $\zeta_{44}^z$  are negative. Further the

values of  $\zeta_{23}^z$  and  $\zeta_{34}^z$  are of the same order. The high values of the constants  $\zeta_{23}^z$  and  $\zeta_{34}^z$  show that the coupling concerned is much stronger. In the case of centrifugal distortion constants presented in table 2, (as expected) the  $D_{JK}$  is found to be negative for this molecule. The thermodynamic functions of  $\text{WO}_3$  molecule are reported in table 3.

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**Table 3** Heat content, free energy, entropy and heat capacity (in cal. deg<sup>-1</sup>, mol<sup>-1</sup>) of  $\text{WO}_3$  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	11.0510	58.9561	14.9900	70.0071
400	12.2638	62.3670	16.5695	74.6312
500	13.2312	65.2196	17.5315	78.4510
600	14.0012	67.7021	18.1473	81.7033
700	14.6250	69.9043	18.5581	84.5293
800	15.1391	71.9070	18.8410	87.0460
900	15.5536	73.6886	19.0415	89.2614
1000	15.9151	75.3541	19.1933	91.2692

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