JOURNAL OF SOLID STATE CHEMISTRY **98**, 350–357 (1992)

Raman Spectra of Hydrogen Molybdenum Bronze, $H_{0.30}MoO_3$

KAZUO EDA

*College of Liberal Arts, Kobe University, Tsurukabuto, Nada,
Kobe 657, Japan*

Received August 26, 1991; in revised form December 2, 1991

The Raman spectra of hydrogen molybdenum bronze, $H_{0.30}MoO_3$, named as Type I, were studied. Four bands observed at 1011, ca. 750, ca. 670, and 452 cm^{-1} were assigned to the Mo–O1, Mo–O3′, Mo–O2′, and Mo–O2 stretching vibrations, respectively. These assignments suggest that the structural change from MoO_3 to Type I induces a shift of the Mo–O1 stretching vibrations to a higher frequency and shifts of the Mo–O3′ and Mo–O2 stretching vibrations to lower frequencies. The frequencies of the Mo–O2′ stretching vibrations were scarcely influenced. These spectral changes were understood on the basis of the changes in the bond length of Type I presented by Dickens *et al.* (*J. Solid State Chem.* **28,** 1185 (1979)).

Introduction

Hydrogen molybdenum bronzes are hydrogen insertion compounds of MoO_3. These compounds retain the Mo–O framework of MoO_3 basically, although their constitution units (Mo–O_6 octahedra) show some rearrangements resulting from the hydrogen insertion. Four phases of these compounds are known to be present (*1–4*). Only the phase with the lowest hydrogen content, $H_{0.23-0.40}MoO_3$, named as Type I, has the same crystal system (i.e., the orthorhombic system) as MoO_3. It is of interest to clarify the relation between change in structure and that in spectral data upon formation of Type I from MoO_3. Previously the author studied IR spectra of Type I and calculated its vibrational frequencies (*5*). In this study, following points were reported: (1) Most of the IR absorption spectra of Type I contain bands attributable to MoO_3 and MoO_3-like structure. (2) MoO_3 shows the bands at 992, 877, 819, 614, and 485 cm^{-1}, while Type I shows those at 1000, 656, 597 and 447 cm^{-1}. (3) The bands observed near 1000 cm^{-1}, in the region 880–650 cm^{-1}, near 600 cm^{-1} and in the region 490–430 cm^{-1} are assigned to the Mo–O1, Mo–O3′, Mo–O2′, and Mo–O2 stretching vibrations, respectively. (4) For the Mo–O3′ stretching bands, the lower frequency shifts of ca. 200 cm^{-1} from MoO_3 to Type I are due to the changes in the Mo–O3 and Mo–O3′ bond lengths.

IR frequencies generally contain some contribution from longitudinal–transverse splitting effects (*6*) and, therefore, do not necessarily coincide with the vibrational frequencies which are calculated by the GF matrix method. Because MoO_3 and Type I have a center of symmetry, their Raman-active modes are IR-inactive and are not influenced by longitudinal–transverse splitting effects. Therefore, Raman data are more advantageous to discuss the relation between the spectral and structural changes. MoO_3 shows sharp and intense Raman bands, and many Raman studies have

0022-4596/92 $5.00

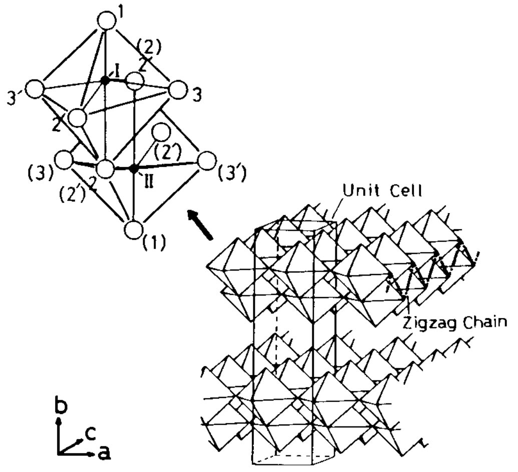

FIG. 1. Structural model for MoO_3 and Type I. Solid and open circles present molybdenum and oxygen atoms, respectively. Numerals in parentheses are given for the molybdenum atom II.

already been performed (*7–12*). However, it is hard to obtain the Raman spectra of Type I because of its dark color and easy degradation to MoO_3 by laser irradiation. We find only the Raman data of Type I previously reported by Schröder and Weitzel (*13*). However, their data closely resemble those of MoO_3 and might be attributed to MoO_3 degraded from Type I by laser irradiation. Therefore, further Raman studies on Type I are needed.

In the present work, the author investigated the Raman spectra of a number of Type I samples prepared from MoO_3 with various particle sizes and finally succeeded in detecting some of true Raman bands due to Type I. The assignments of these bands were carried out by comparison with the vibrational frequencies obtained by my previous calculation (*5*) based on the sheet model (*10, 11*). Then, differences in Raman frequency between MoO_3 and Type I were discussed.

Background

MoO_3 and Type I have the Mo–O framework, shown in Fig. 1, which consists of the sheets of $Mo–O_6$ octahedra sharing edges (O2–O2′) (*14–16*). Oxygen atoms in the framework are divided into three groups by bonding types with the Mo atoms. Hydrogen atoms in Type I occupy the sites on the intrasheet zigzag chain of the O3 and O3′ atoms and form OH groups with these oxygen atoms (*17–19*). The unit cells of MoO_3 and Type I crystals consist of the unit sections, shown on the upper left side of Fig. 1, of two sheets. The crystal data of MoO_3 were given by Kihlborg (*14*), while those of Type I were reported by Wilhelmi (*15*) and Dickens *et al.* (*16*). According to them, Mo–O bond lengths of MoO_3 and Type I are as shown in Fig. 2. The data for Type I reported by the two groups are slightly different from each other.

The O3 atom in a unit cell corresponds to the O3′ atom in the neighboring unit cell (Fig. 1), i.e., the O3 and O3′ atoms are treated as the same atom under the unit cell group analysis. Therefore, it is unnecessary to consider the Mo–O3 stretching vibration in addition to the Mo–O3′ stretching vibration. The O3′ atom receives the contribution of force constant f_{O3} arising from the Mo–O3 bond, and the Mo–O3′ stretching vibration is regarded as a vibration of the O3′ (or O3) atom joined with two Mo atoms by two different springs whose force constants are f_{O3} and $f_{O3'}$, respectively. The f_{Oi} indicate stretching force constants of the Mo–Oi bonds. The Mo–O2′ stretching vibration is, of course, a vibration of the O2′ atom joined by two equal springs of force constant $f_{O2'}$. In the previous study (*5*), the author noted these vibrations as Mo–O3, 3′–Mo, and Mo–O2′–Mo stretching vibrations, respectively, but in this study these are simply noted as Mo–O3′ and Mo–O2′ stretching vibrations, respectively.

Experimental

Materials and characterization. Type I samples were prepared from MoO_3 by the

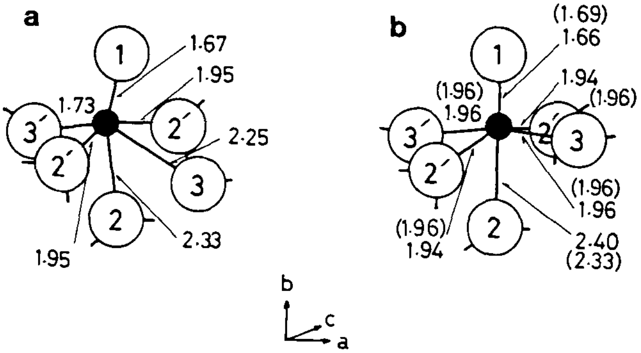

FIG. 2. Schematic model of the octahedra for (a) MoO_3 and (b) Type I. Bond lengths for MoO_3 are after Kihlborg (*14*). Those for Type I after Dickens *et al.* (*16*) and Wilhelmi (*15*) are shown without and with parentheses, respectively.

previously mentioned method (*5*). Four kinds of MoO_3 were used: (1) Wako-Junyaku grade 1 MoO_3 produced by a wet chemical process; (2) Climax Molybdenum Co. grade L MoO_3 produced by a sublimation process; and (3), (4) their heated ones at suitable temperatures between 773 and 973 K with grown-up particles. The Type I sample prepared from the (2) MoO_3 was found out to be the best one for Raman measurements (*20*).

The sample was identified as Type I by the X-ray diffraction method (*21*). The X-ray diffraction patterns were measured by a Rigaku RINT 1200M diffractometer. The hydrogen content in Type I was determined by the method of Choain and Marion (*22*). The typical composition of the sample was $H_{0.30}MoO_3$.

Raman measurements. The Raman spectra were measured on a Spex Ramalog 5 spectrophotometer equipped with a Hamamatsu Photonics R 94302 photomultiplier by step scanning. For excitation 4880 and 5145 Å lines of an Ar^+ laser were employed. The Type I sample was pressed into disks (15 wt% in KBr). To avoid the degradation of the samples by laser irradiation, the disks were rotated at a speed of ca. 3000 rpm by a spinning cell.

Results

The Raman spectra of MoO_3 obtained with 20 mW power of the 4880 Å excitation line are shown in Fig. 3. Figure 3a was recorded with a spectral resolution of 3 cm^{-1}. Seventeen bands are observed at 995, 819, 666, 471, 378, 366, 338, 291, 283, 246, 217, 197, 159, 129, 117, 100, and 84 cm^{-1}. These frequencies coincide with previously reported data (*7–12*). For comparison with the spectra of Type I, Fig. 3b was obtained with a spectral resolution of 12 cm^{-1}.

Figure 4 shows Raman spectra obtained from the Type I sample with various output powers of the 4880 Å excitation line at an integration time of 1 sec. The spectrum obtained with 20 mW laser power (Fig. 4a) was very noisy and, therefore, was subjected to improvement in its signal-to-noise ratio by taking the average of five measurements. (A new sample pellet was used for each measurement.) It shows four bands at 1011, ca. 750, ca. 670, and 452 cm^{-1}. The spectrum obtained with 50 mW laser power (Fig. 4b) was also noisy and was smoothed by a 3-points averaging operation. It also shows the above four bands of weaker intensities with an additional band at 819 cm^{-1}. The band observed at ca. 750 cm^{-1} in Fig. 4a shifts slightly to the higher frequency side

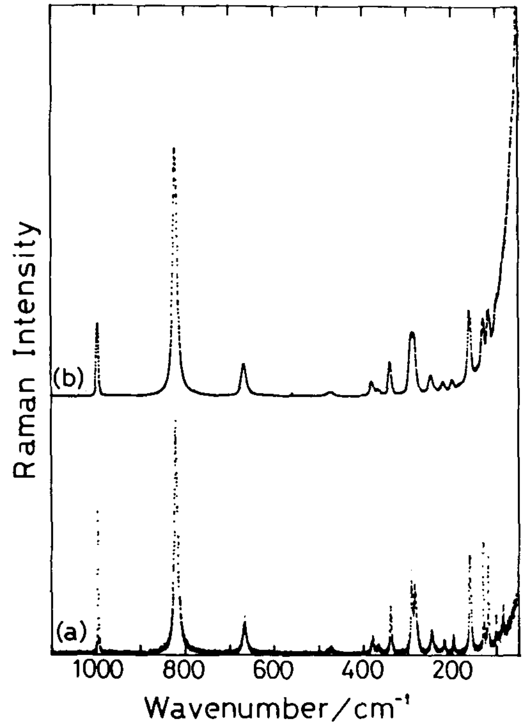

FIG. 3. Raman spectra of MoO_3 obtained with a spectral resolution of (a) 3 cm^{-1} and (b) 12 cm^{-1} (the 4880 Å excitation line with output power of 20 mW, scanning interval 0.2 cm^{-1}, integration time 0.1 sec).

in Fig. 4b. The spectrum obtained with 100 mW laser power (Fig. 4c) shows one more additional band at 995 cm^{-1}. The band at ca. 750 cm^{-1} further shifts to the higher frequency side. With 400 mW laser power (Fig. 4d), two more additional bands appear at 337 and 283 cm^{-1}. In this spectrum the band near 750 cm^{-1} is observed at 770 cm^{-1}. The relative intensities of the 995 and 819 cm^{-1} bands to the bands at 1011 and 452 cm^{-1} apparently increase with the increase in the laser power. The relative intensity of the band around 670 cm^{-1} also increases by 400 mW power excitation (Fig. 4d). It seems therefore that a further additional band overlaps with the original band around 670 cm^{-1}. The frequencies of all the additional bands coincide with those of MoO_3 shown in Fig. 3.

The spectrum obtained by a long time measurement (integration time 5 sec) with 20 mW power shows the additional band at 819 cm^{-1}. The 5145 Å excitation bears the same results as the 4880 Å excitation.

Discussion

The bands attributed to Type I. Since, as mentioned above, the additional bands coincide in frequency with the MoO_3 bands, they are undoubtedly ascribed to MoO_3 degraded from Type I by laser irradiation. At the same time, Fig. 4a obtained by the short-

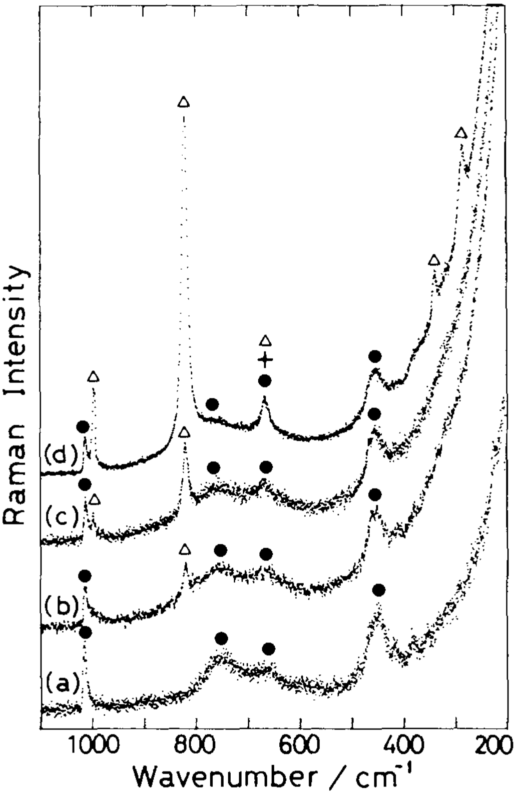

FIG. 4. Raman spectra of Type I obtained by the 4880 Å excitation line with output power of (a) 20 mW, (b) 50 mW, (c) 100 mW, and (d) 400 mW (scanning interval 0.5 cm^{-1}, integration time 1 s, spectral resolution 12 cm^{-1}). ●, Type I band; Δ, MoO_3 band.

TABLE I

RAMAN FREQUENCIES (cm^{-1}) AND THEIR ASSIGNMENTS OF MoO_3 AND TYPE I

MoO_3		Type I		
Observed	Assign.	Observed	Calculated	Assign.
995	ν_{MoO1}	1011	993	ν_{MoO1}
819	$\nu_{\mathrm{MoO3'}}$	ca. 750[a]	649	$\nu_{\mathrm{MoO3'}}$
666	$\nu_{\mathrm{MoO2'}}$	ca. 670	654	$\nu_{\mathrm{MoO2'}}$
471	ν_{MoO2}	452	461	ν_{MoO2}
378	Angle deformation			
366		—	263	Angle deformation
338		—	206	
291				
283		—	186	
217		—	335	
246				
197		—	267	
159		—	155	
129				
117		—	85	
100				
84		—	53	

[a] Broad band.

est time measurement with the lowest laser power is believed to be the characteristic Raman spectrum of Type I, and the four bands at 1011, ca. 750, ca. 670, and 452 cm^{-1} are the vibration bands of the Type I crystal.

Dickens *et al.* have observed the band at 1267 cm^{-1} due to the Mo–O–H deformation of Type I by inelastic neutron scattering (*16*) and by IR spectroscopy (*23*). However, no band was observed in the same frequency region in the present work. Raman spectra below 200 cm^{-1} were also examined, but no band attributable to Type I could be observed.

Assignment of the bands. The observed frequencies of MoO_3 and Type I are summarized in Table I. For the Type I bands, the previously calculated values (*5*) are also shown.

Assignments of the MoO_3 bands based on the calculated frequencies have been reported by Beattie *et al.* (*10*) and by Py and Maschke (*11*). According to them, the bands at 995, 819, 666, and 471 cm^{-1} were attributed to the Mo–O1, Mo–O3′, Mo–O2′, and Mo–O2 stretching vibrations, respectively. The bands below 400 cm^{-1} are ascribed to angle-deformation vibrations.

For Type I, only the four bands are observed. The frequencies of 1011 and 452 cm^{-1} are in reasonable agreement with the calculated values and can be ascribed to the Mo–O1 and Mo–O2 stretching vibrations, respectively. The observed frequency of ca. 670 cm^{-1} is close to the calculated values of 649 and 654 cm^{-1} which have been attributed to the Mo–O3′ and Mo–O2′ stretching vibrations, respectively. However, there is no calculated value near 750 cm^{-1}. The long time measurements indicate that even small laser power (20 mW) irradiation causes the degradation. Therefore, even Fig. 4a may contain the contribution of mild degradation (i.e., partial removal of the hydrogen atom), although it does not show any MoO_3 bands which indicate hard degradation. The direct attachment of hydrogen atoms to the O3 and O3′ atoms in Type I, mentioned in the Background section, results in the large changes in length of the Mo–O3 and Mo–O3′ bonds (Fig. 2). The mild degradation of Type I may give rise to a distortion in length of the same bonds. The mildly degraded Type I is regarded as an intermediate between Type I and MoO_3, and the Mo–O3 and Mo–O3′ bond lengths in such samples are expected to have intermediate values between their original values in pure Type I and MoO_3. In such a case, the Mo–O3′ stretching vibration may appear as a broad band between ca. 650 (for Type I) and 819 cm^{-1} (for MoO_3). The broad band at ca. 750 cm^{-1} may correspond to such a band. The above-mentioned shift of this band to the higher frequency side by larger power excitations (Fig. 4) can be understood considering the increase in the degree of degradation arising from the larger power irradiation. Therefore, this band can be ascribed to the Mo–O3′ stretching vibration. Because the hydrogen atom does not directly attach to the O1, O2, and O2′ atoms, the effects of the mild degradation to the Mo–O1, Mo–O2, and Mo–O2′ stretching vibrations are supposed to be small. Consequently, the band at ca. 670 cm^{-1} is assigned to the Mo–O2′ stretching vibration.

Spectral changes from MoO_3 to Type I. The frequency changes of the Raman bands with formation of Type I from MoO_3 are summarized in Table II, together with those of the IR bands. The frequency shift from 819 cm^{-1} of MoO_3 to 750 cm^{-1} of Type I observed in the present work is due to the changes in the Mo–O3 and Mo–O3′ bond lengths. This lower frequency shift has been predicted by the previous calculation of vibrational frequencies (*5*), in which the changes in force constant of the Mo–O3 and Mo–O3′ bonds were considered (*24*). With respect to the lengths of these bonds, the data for Type I by Wilhelmi (*15*) and Dickens *et al.* (*16*) coincide with each other. On the formation of Type I from MoO_3, the Mo–O3′ bond becomes lengthened from 1.73 to 1.96 Å, while the Mo–O3 bond is shortened from 2.25 to 1.96 Å. The changes in the Mo–O3 and Mo–O3′ bond lengths are 0.29 and −0.23 Å, respectively. They are comparable in the absolute value, but have opposite signs to make opposite frequency shifts. The above shift to a lower frequency is easily understood by considering that a shorter bond makes a larger change in the force constant than a longer bond, because the force constant increases steeply as the bond length decreases (*25, 26*). With respect to the stretching vibrations of the Mo–O bonds whose lengths are different between the data for Type I by Wilhelmi (*15*) and Dickens *et al.* (*16*), the Raman frequency changes [Type I − MoO_3] for the Mo–O1, Mo–O2′, and Mo–O2 stretching vibrations are 16, about 4, and −19 cm^{-1}, respectively (Table II). According to the data of Dickens *et al.*, the changes in the Mo–O1, Mo–O2′, and Mo–O2 bond lengths are −0.01, −0.01, and 0.07 Å, respectively, while according to those of Wilhelmi are 0.02, 0.01, and 0 Å, respectively (Fig. 2). The changes in Raman frequency can be interpreted by the former data (*27*), and, thus, they are suitable for the bond lengths of Type I as far as the present results are concerned.

Further refinement of the force constants used in the previous calculation (*5*) could not be performed because of the small number of the observed bands, and therefore accurate estimation of the changes in force constant with the bond-length changes could not be achieved in the present work.

Comparison between Raman and IR data. The IR frequency changes [Type I − MoO_3] for the Mo–O1, Mo–O3′, Mo–O2′, and Mo–O2 stretching vibrations are 8, −221 (or −163), −17, and −38 cm^{-1}, respectively (Table II). For both MoO_3 and Type I,

TABLE II

CHANGES IN BAND FREQUENCIES (cm^{-1}) WITH FORMATION OF Type I FROM MoO_3

	Raman			IR		
Mode	MoO_3	Type I	$\Delta\nu$	MoO_3	Type I	$\Delta\nu$
ν_{MoO1}	995	1011	16	992	1000	8
$\nu_{MoO3'}$	819	750[a]	−69	877 819	656	−221 −163
$\nu_{MoO2'}$	666	670	4	614	597	−17
ν_{MoO2}	471	452	−19	485	447	−38

Note. $\Delta\nu_{\text{Type I}} - \nu_{MoO_3}$.

[a] Broad band.

the frequencies calculated by the GF matrix method for the IR-active Mo–O stretching bands resemble those for the corresponding Raman-active Mo–O stretching bands, respectively (*5, 10, 26*). This fact indicates that the changes in force constant owing to the structural change from MoO_3 to Type I result in similar frequency changes for both IR and Raman bands. Thus, it seems that the observed differences between the changes in the IR and Raman frequencies are due to longitudinal–transverse splitting effects (*24*).

Acknowledgments

The author thanks Professor T. Takenaka, Associate Professor S. Hayashi, Dr. J. Umemura, and Professor N. Sotani for their useful discussions.

References

1. O. Glemser and G. Lutz, *Z. Anorg. Allg. Chem.* **264,** 17 (1951).
2. O. Glemser, G. Lutz and G. Meyer, *Z. Anorg. Allg. Chem.* **285,** 173 (1956).
3. J. J. Birtill and P. G. Dickens, *Mater. Res. Bull.* **13,** 311 (1978).
4. N. Sotani, K. Eda, M. Sadamatu, and S. Takagi, *Bull. Chem. Soc. Jpn.* **62,** 903 (1989).
5. K. Eda, *J. Solid State Chem.* **83,** 292 (1989).
6. P. M. A. Sherwood, "Vibrational Spectroscopy of Solids," Chap. 4, Cambridge Univ. Press, London/New York (1972).
7. I. R. Beattie and T. R. Gilson, *Proc. R. Soc. London A* **307,** 407 (1968).
8. I. R. Beattie and T. R. Gilson, *J. Chem. Soc. A*, 2322 (1969).
9. R. Mattes and F. Schröder, *Z. Naturforsch. B 24,* 1095 (1969).
10. I. R. Beattie, N. Cheetham, M. Gardner, and D. E. Rogers, *J. Chem. Soc. A*, 2240 (1971).
11. M. A. Py and K. Maschke, *Physica B* **105,** 370 (1981).
12. S. Mohan and K. G. Ravikumar, *Bull. Soc. Chim. Fr.*, 267 (1983).
13. F. A. Schröder and H. Weitzel, *Z. Anorg. Allg. Chem.* **435,** 247 (1977).
14. L. Kihlborg, *Ark. Kemi.* **21,** 357 (1963).
15. K. A. Wilhelmi, *Acta Chem. Scand.* **23,** 419 (1969).
16. P. G. Dickens, J. J. Birtill, and C. J. Wright, *J. Solid State Chem.* **28,** 185 (1979).
17. R. C. T. Slade, T. K. Halstead, and P.G. Dickens, *J. Solid State Chem.* **34,** 183 (1980).
18. Cl. Ritter W. Müller-Warmuth, and R. Schöllhorn, *J. Chem. Phys.* **83,** 6130 (1985).
19. N. Sotani, K. Eda, and M. Kunitomo, *J. Chem. Soc. Faraday Trans.* **86,** 1583 (1990).
20. The Type I sample prepared from the (1) MoO_3 was severely degraded by laser irradiation, while the Type I samples from the (3) and (4) MoO_3 were not severely degraded, but tended to contain MoO_3 in spite of careful preparation.
21. Raman intensities of MoO_3 bands are much larger than those of Type I bands. If Type I samples have a small trace of MoO_3 peaks in their X-ray diffraction patterns, they exhibit MoO_3 bands of comparable intensities in their Raman spectra.

22. C. Choain and F. Marion, *Bull. Soc. Chim. Fr.*, 212 (1963).

23. P. G. Dickens, S. J. Hibble, and G. S. James, *Solid Sate Ionics* **20,** 213 (1986).

24. For the Mo–O3′ stretching Raman bands, it is necessary to recall the above-mentioned contribution of the mild degradation by laser irradiation.

25. F. A. Cotton and R. M. Wing, *Inorg. Chem.* **4,** 867 (1965).

26. M. A. Py, Ph.D. Thesis, Swiss Federal Institute of Technology, Lausanne, Switzerland (1980).

27. For the Mo–O2 stretching bands the potential energy distribution to the Mo–O2 stretching force constant is important but not absolutely predominant (ca. 40%) (*5, 10, 26*). Therefore, the frequency change for these bands may considerably contain the contributions of the changes in some angle-deformation force constants.