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Infrared Spectra of Hydrogen Molybdenum Bronze, $H_{0.34}MoO_3$

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The author has calculated the fundamental vibrational frequencies for Type-I (bronze) and has studied bronzes with various hydrogen contents by means of IR spectroscopy and X-ray diffraction. The calculation has been carried out only on the Mo–O framework, by ignoring hydrogen atoms, because of the low occupancy of hydrogen sites and the high mobility of hydrogen atoms. The frequencies of the modes attributed to Mo–O[3,3′]–Mo stretching vibrations for the bronze are about 650 cm^{-1}, while those for MoO_3 are about 820 cm^{-1}. This difference has been explained as the result of changes in bond lengths of Mo–O[3] and Mo–O[3′] as obtained by calculation. Moreover, it has been confirmed that bands in the region 900–800 cm^{-1}, which are involved in previous spectroscopic data for the bronze, are associated with the MoO_3 structure.

Introduction

Hydrogen molybdenum bronzes, H_xMoO_3 ($0.23 < x \leqq 2.0$), are hydrogen insertion compounds of rhombic MoO_3 which are prepared by chemical reduction of MoO_3 in Zn/HCl. They form four distinct phases (*1*); H_xMoO_3 ($0.23 < x < 0.40$), named Type-I for convenience, is the first member of the series.

Type-I has the same orthorhombic Mo–O framework as that of MoO_3 (*1*). However, a minor rearrangement in the Mo–O framework has been observed when Type-I is formed by the insertion of hydrogen atoms into MoO_3 (*1, 2*). It is of great interest to clarify the relationship between spectroscopic changes and the rearrangement. Several spectroscopic studies for Type-I (*3–5*) have been carried out. Ohno *et al.* (*3*) have already reported on an interesting relation between the change in frequency of a Mo–O[1] stretching vibration and the change in hydrogen content for Type-I. They have studied the changes in the region 1000–800 cm^{-1} of IR spectra of $H_{0.3}MoO_3$ on heating *in vacuo*. Schröder and Weitzel (*4*) have studied Type-I by IR and Raman spectroscopy and have attempted to show the structural differences between Type-I and MoO_3. However, no discussion of the calculation of vibrations based on structural data was provided in these studies. The fundamental vibrational frequencies of MoO_3 have been calculated from structural data on the basis of an approximation proposed by Beattie *et al.* (*6*) and Py and Maschke (*7*). The structure of Type-I has been characterized by means of powder X-ray diffraction and powder neutron diffraction (*2, 8*). This bronze has the same layered structure as MoO_3. Thus, the fundamental vibrations of Type-I can be estimated by applying the approximation of Beattie *et al.*

In the present work, the author has cal-

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culated the vibrational frequencies and potential energy distributions among internal coordinates for Type-I. On the basis of these results, spectroscopic data have been discussed.

Calculation of Vibrational Frequencies and Potential Energy Distributions

Basis of Calculation

Layered structures indicate the existence of weak interlayer and strong intralayer interactions (*6, 7, 9*). Thus a material with such a structure can be treated as an aggregate of infinite sheet "molecules." For MoO_3 the unit cell contains sections of two different sheets. This section constitutes a primitive unit cell of the individual sheet. The individual sheets are identical with each other. Thus, Beattie *et al.* have calculated the vibrations of one sheet, that is, those of the section of the sheet as those of MoO_3 by assuming that correlation splitting effects are small (*6*). Type-I has a layered structure and its unit cell is similar to that of MoO_3. Therefore, as mentioned above, the estimation of fundamental vibrations of Type-I can be achieved by a calculation based on the approach of Beattie *et al.* However, in this calculation there is the important problem of how to deal with hydrogen atoms, because the average occupancy of hydrogen sites is very small, for example, 0.15 for $H_{0.3}MoO_3$ (*8, 10*). Vibrational modes of $H_{0.34}MoO_3$ concerning hydrogen atoms have been observed at liquid nitrogen temperature by the inelastic neutron scattering method (*8*). Although many IR studies have been performed on Type-I at room temperature, such modes have not been observed (*3–5*). According to NMR study (*10*) of $H_{0.36}MoO_3$, a modulation of the dipolar interaction between nuclear magnetism of hydrogen atoms by hydrogen diffusion occurs at $T > 215$ K. It is predicted that the inserted hydrogen atoms have a considerable mobility at room temperature. We have studied a series of H_xMoO_3 by NMR and have obtained evidence that even in Type-I hydrogen atoms move with a high mobility at room temperature (*11*). Because of this high mobility and the low occupancy of hydrogen sites, it has been assumed that the hydrogen atoms provide only a driving force for the rearrangement of the Mo–O framework, but do not behave as elements of fundamental vibrations. Thus, only vibrational frequencies pertaining to the Mo–O framework have been calculated.

Calculation

The calculation has been carried out according to the approach by Beattie *et al.* Vibrational eigenvalues have been determined directly from GF matrix which was expressed in terms of a symmetrized mass-weighted Cartesian coordinate system. This symmetrized coordinate system has been obtained by considering the projection operator (*12*). The internal coordinates are the same as those proposed for MoO_3 by Beattie *et al.* (*6*), as shown in Fig. 1. The Cartesian coordinates of atoms for $D_{0.36}MoO_3$, which were obtained directly from powder neutron analysis (*8*), have been used for the Type-I compound because a powder neutron analysis for Type-I may not have adequate precision and the cell parameters of $H_{0.34}MoO_3$ are almost equal to those of $D_{0.36}MoO_3$ (*8*). The set of cartesian coordinates is given in Table I. Several studies (*6, 7, 13, 14*) to evaluate force constants have been reported. Py and Maschke (*7*) have refined the force constants proposed by Beattie *et al.* (*6*) and have succeeded in the calculation of vibrational frequencies of MoO_3 which are in excellent agreement with Raman data. In this work, the stretching force constants were evaluated on the basis of those of MoO_3 which had been given by Py and Maschke. On the other hand, angle-deformation force

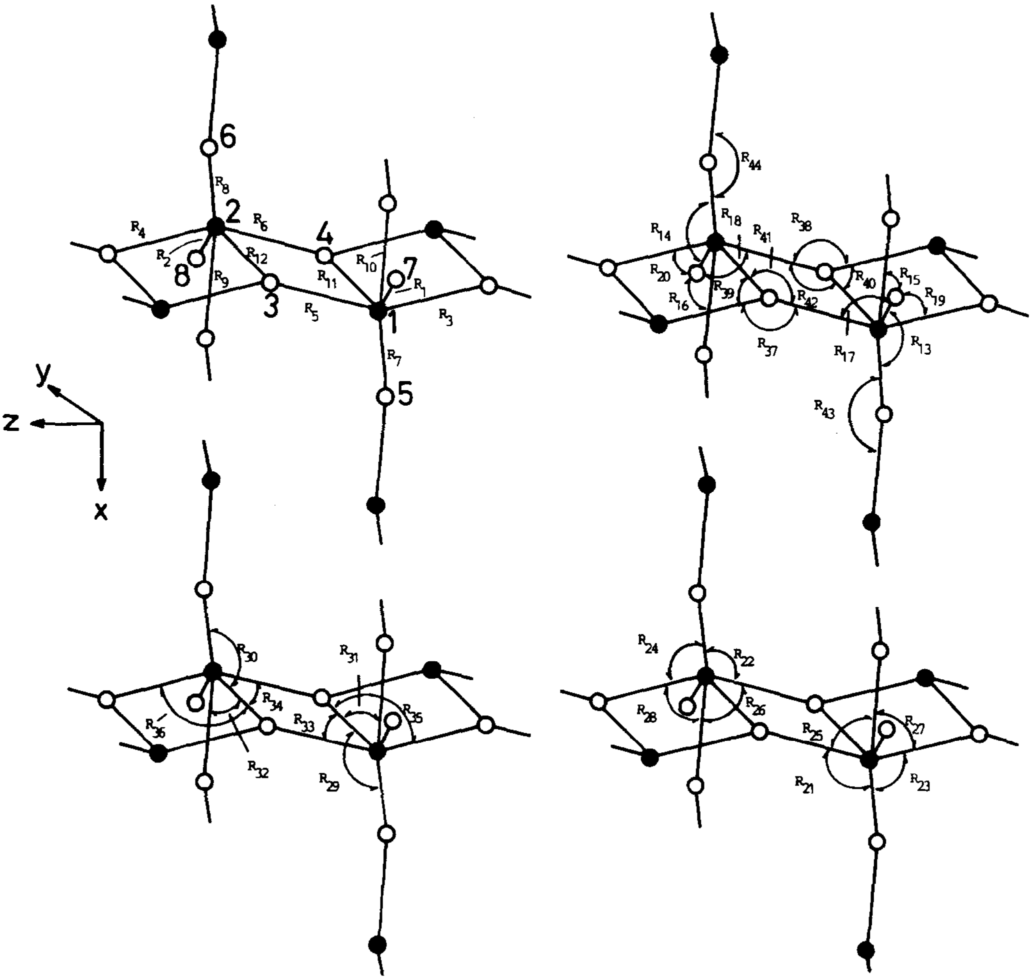

FIG. 1. Internal coordinates of the Mo–O framework; (○) oxygen atoms and (●) molybdenum atoms.

constants were evaluated according to those of MoO_3 by Beattie *et al.* (*6*), because the selection of internal angle-deformation coordinates in this work is same as that by Beattie *et al.* and not those of Py and Maschke. The calculated results by Beattie *et al.* for angle-deformation modes of MoO_3 agreed reasonably well with Raman data. The set of employed force constants is shown in Table II. To confirm the validity of the calculation for Type-I, a calculation of vibrational frequencies for MoO_3 has also been carried out. Here the internal coordinates and the Cartesian coordinates of atoms proposed by Beattie *et al.* were used, but force constants have been used in the same manner as for Type-I compounds. The values by Py and Maschke for stretching force constants and those by Beattie *et al.* for angle-deformation force constants were used.

Experimental

Materials. The preparation and identification of Type-I have been described previ-

TABLE I

CARTESIAN COORDINATES (Å) OF TYPE-I

Atom number[a]	Cartesian coordinates x	y	z
1	0	1.46469	0.93425
2	0	−1.46469	2.80275
3	0	0.94550	2.80275
4	0	−0.94550	0.93425
5	1.9475	1.21002	0.93425
6	−1.9475	−1.21002	2.80275
7	0	3.14324	0.93425
8	0	−3.14324	2.80275

[a] See Fig. 1.

ously (*5*, *15*, *16*). The maximum hydrogen content of all samples was $x = 0.34$. Type-I with the minimum hydrogen content ($x = 0.21$) was obtained by shortening the exposure of MoO_3 to Zn/HCl. Samples with several hydrogen contents (formulated as $H_x MoO_{2.83+0.5x}$, $0 < x < 0.34$) were prepared by heating $H_{0.34}MoO_3$ at suitable temperatures *in vacuo*. The composition was determined by thermogravimetry (*15*) and by the method of Choain and Marion (*17*).

IR spectroscopy. Samples were pressed into disks (ca. 0.5 wt% in KBr). All spectra were recorded at room temperature by using a JASCO 701G spectrophotometer.

Powder X-ray diffraction method. Samples were mixed with an internal standard (ca. 5 wt% Si powder). All powder X-ray diffraction patterns were obtained by using a Rigakudenki Geiger D-1 FLEX diffractometer with Cu*Kα* radiation.

Results and Discussion

Calculated Vibrations

The vibrational frequencies calculated for Type-I and MoO_3 are given in Table III. The last column in the table specifies the vibrational frequencies calculated by Beattie *et al.* for MoO_3 (*6*). The calculated fre-

TABLE II

PRIMARY FORCE CONSTANTS ASSUMED FOR TYPE-I

Force constant number	Internal[a] coordinate numbers	Force constant[b]
1	$R_{1,2}$	7.915
2	$R_{3,4,5,6}$	1.710
3	$R_{7,8,9,10}$	1.710
4	$R_{11,12}$	0.800
5	$R_{13,14,15,16}$	0.800
6	$R_{17,18,19,20}$	0.800
7	$R_{21,22,23,24,25,26,27,28}$	0.300
8	$R_{29,30,31,32}$	0.200
9	$R_{33,34,35,36}$	0.200
10	$R_{37,38}$	0.300
11	$R_{39,40,41,42}$	0.300
12	$R_{43,44}$	0.300

[a] See Fig. 1.

[b] Bond-stretching force constant (1–4) (mdyn $Å^{-1}$); angle-deformation force constant (5–12) in mdyn Å rad^{-2}.

TABLE III

CALCULATED VIBRATIONAL FREQUENCIES (cm^{-1}) FOR TYPE-I AND MoO_3

Type-I Sym.	Freq.	Assign.	MoO_3 Sym.	This work Freq.	Beattie *et al.* Freq.
Ag	155		Ag	57	57
	335			151	151
	461			219	219
	993	V(MoO1)		275	275
B1g	53			370	370
	206			453	453
	263			821	846
	649	V(MoO3,3′Mo)		994	917
B3g	85		Bg	87	87
	186			218	218
	267			265	265
	654	V(MoO2′Mo)		647	646
B1u	184		Au	217	217
	260			259	259
	656	V(MoO2′Mo)		649	648
B2u	324		Bu	202	202
	492			288	289
	994	V(MoO1)		362	363
B3u	210			485	484
	264			821	846
	649	V(MoO3,3′Mo)		994	918

Note. V indicates a stretching vibration.

TABLE IV

Potential Energy Distributions among the Force Constants for Type-I

Symmetry species	Calculated frequency (cm^{-1})	Force constant number[a] 1	2	3	4	5	6	7	8	9	10	11	12
Ag	155	0.003	0.074	0.004	0.586	0.025	0.119	0.000	0.006	0.030	0.089	0.045	0.019
	335	0.005	0.002	0.060	0.045	0.428	0.003	0.024	0.107	0.001	0.002	0.001	0.321
	461	0.001	0.130	0.000	0.366	0.001	0.209	0.003	0.000	0.052	0.157	0.079	0.001
	993	0.991	0.001	0.000	0.002	0.001	0.001	0.000	0.000	0.000	0.001	0.000	0.001
B1g	53	0.000	0.000	0.000	0.000	0.006	0.000	0.134	0.860	0.000	0.000	0.000	0.000
	206	0.000	0.000	0.000	0.000	0.031	0.000	0.829	0.140	0.000	0.000	0.000	0.000
	263	0.000	0.000	0.017	0.000	0.948	0.000	0.035	0.000	0.000	0.000	0.000	0.000
	649	0.000	0.000	0.983	0.000	0.015	0.000	0.001	0.000	0.000	0.000	0.000	0.000
B3g	85	0.000	0.067	0.000	0.000	0.000	0.017	0.040	0.000	0.350	0.000	0.525	0.000
	186	0.000	0.002	0.000	0.000	0.000	0.051	0.920	0.000	0.010	0.000	0.016	0.000
	267	0.000	0.017	0.000	0.000	0.000	0.902	0.038	0.000	0.017	0.000	0.026	0.000
	654	0.000	0.913	0.000	0.000	0.000	0.031	0.001	0.000	0.022	0.000	0.033	0.000
B1u	184	0.000	0.000	0.000	0.000	0.000	0.030	0.970	0.000	0.000	0.000	0.000	0.000
	260	0.000	0.032	0.000	0.000	0.000	0.938	0.029	0.000	0.000	0.000	0.002	0.000
	656	0.000	0.905	0.000	0.000	0.000	0.032	0.001	0.000	0.009	0.000	0.052	0.000
B2u	324	0.002	0.003	0.063	0.010	0.445	0.005	0.021	0.111	0.001	0.004	0.002	0.334
	492	0.011	0.119	0.001	0.389	0.010	0.192	0.005	0.002	0.048	0.144	0.072	0.007
	994	0.988	0.001	0.000	0.004	0.001	0.002	0.000	0.000	0.000	0.001	0.001	0.001
B3u	210	0.000	0.000	0.000	0.000	0.077	0.000	0.757	0.166	0.000	0.000	0.000	0.000
	264	0.000	0.000	0.017	0.000	0.907	0.000	0.062	0.014	0.000	0.000	0.000	0.000
	649	0.000	0.000	0.983	0.000	0.015	0.000	0.001	0.000	0.000	0.000	0.000	0.000

[a] See Table II.

quencies for MoO_3 in this work are in good agreement with Raman data (*6*, *7*). This indicates the validity of the calculation. The calculated potential energy distributions among the force constants for Type-I are shown in Table IV.

The calculated vibrations may be assigned on the basis of the potential energy distributions. The schematic models of oxygen atoms surrounding a molybdenum atom for Type-I and MoO_3 are shown in Fig. 2. In Table III, the modes corresponding to the same vibrations for Type-I and MoO_3 are shown by using arrows. Most of the frequencies associated with similar modes for both Type-I and MoO_3 are close to each other, whereas there exist appreciable differences in the frequencies of the modes assigned to Mo–O[3,3′]–Mo stretching vibrations. According to the previous reports (*2*, *8*, *18*), the bond-lengths of Mo–O[2′], Mo–O[3], Mo–O[3′], Mo–O[2], and Mo–O[1] in MoO_3 are 1.95, 2.25, 1.73, 2.33, and 1.67 Å, respectively; in Type-I, those of Mo–O[2′], Mo–O[3], Mo–O[3′], Mo–O[2], and Mo–O[1] are 1.94, 1.96, 1.96, 2.40, and 1.66 Å, respectively. Only the bond-lengths of Mo–O[3] and Mo–O[3′] are greatly affected by the insertion of hydrogen atoms. These are the most characteristic differences in structure between Type-I and MoO_3. The calculated results have reflected these structural changes. Another interesting difference occurs in the angle of Mo–O[1] against the sheet plane. In Type-I the Mo–O[1] bonds are normal to the plane. On the other hand, those of MoO_3 are at an inclined angle. However, there is no large difference between Type-I and MoO_3 in the frequencies of the modes assigned to the stretching vibration of Mo–O[1] (Table III); this may result from neglect of interlayer interactions.

IR Spectra of Type-I

The IR spectra and the X-ray diffraction patterns of both $H_{0.34}MoO_3$ and $H_{0.21}MoO_3$ are shown in Figs. 3 and 4, respectively. The IR results (Fig. 3) and the previous spectroscopic data for Type-I (*3*–*5*) are

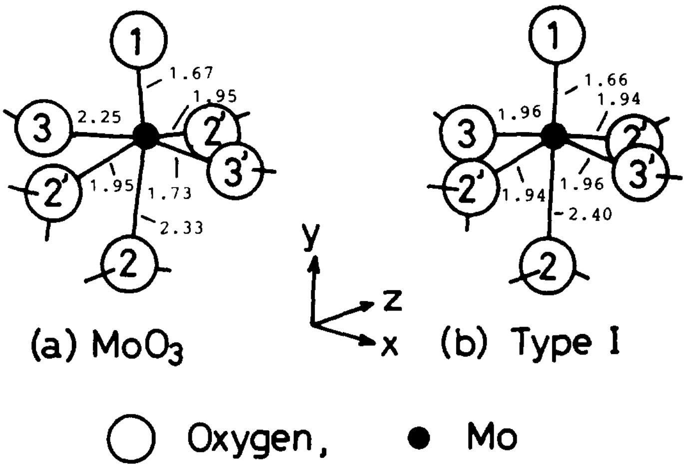

FIG. 2. Schematic models of coordination oxygen atoms surrounding the molybdenum atom; (a) MoO_3 and (b) Type-I. Numbers shown are in angstroms.

summarized in Tables V and VI, respectively. The spectrum of $H_{0.34}MoO_3$ is comparable to that of Type-I reported by Ohno *et al.* The observed frequencies of 1000, 656, 597, and 447 cm^{-1} for $H_{0.34}MoO_3$ are in good agreement with the calculated values of 994, 649, 656, and 492 cm^{-1} for Type-I (Table III). The spectrum of $H_{0.21}MoO_3$ is comparable to that of Type-I by Sotani *et al.* and is nearly the same as that of $H_{0.34}MoO_3$, but contains a band at 855 cm^{-1} not present in $H_{0.34}MoO_3$. The X-ray diffraction patterns of these two bronzes are the same. H_xMoO_3 is a metallic conductor which gives rise to a loss of structure in the IR spectra. The conductivity increases with increasing x. Thus, the appearance of the band at 855 cm^{-1} may be the result of a lower conductivity. On the other hand, Schröder and Weitzel reported other bands in Type-I. The band at 855 cm^{-1} in Fig. 3 and the bands by Schröder and Weitzel have frequencies which can be attributed to MoO_3. Because Type-I is rather unstable, these bands may result from contamination by MoO_3. In order to investigate the IR spectra of Type-I, samples with several hy-

TABLE V

OBSERVED BAND FREQUENCIES (cm^{-1}) OF SAMPLES

$H_{0.34}MoO_3$	$H_{0.21}MoO_3$	MoO_3	$MoO_{2.83}$	Assign.
1000	1001		1000	
		992[a]	983[a]	V(MoO1)
			899[a]	
	855[a]	877[a]	863[a]	
		819[a]	819[a]	V(MoO3,3'Mo)
656	677			
		614[a]	603[a]	
597	590			V(MoO2'Mo)
		485[a]	480[a]	
447	436			

Note. V indicates a stretching vibration.

[a] Indicates a band attributed to MoO_3 or MoO_3-like structure.

TABLE VI

PREVIOUS SPECTROSCOPIC DATA FOR TYPE-I

F. A. Schröder and Weitzel			Ohno *et al.*		Sotani *et al.*	
IR	Assign.	Raman	IR	Assign.	IR	Assign.
1004	V(MoO1)	990	999	V(MoO1)	1004	V(MoO1)
873	V(MoO3)				835	
820	V(MoO2)	812				
677	V(MoO3)	660	650		626	
642						
590			590		569	
445	V(MoO3)		430		428	
370	d(O1MoO3)				355	

Note. V and d indicate a stretching vibration and a bending vibration, respectively. Table is shown in cm^{-1}.

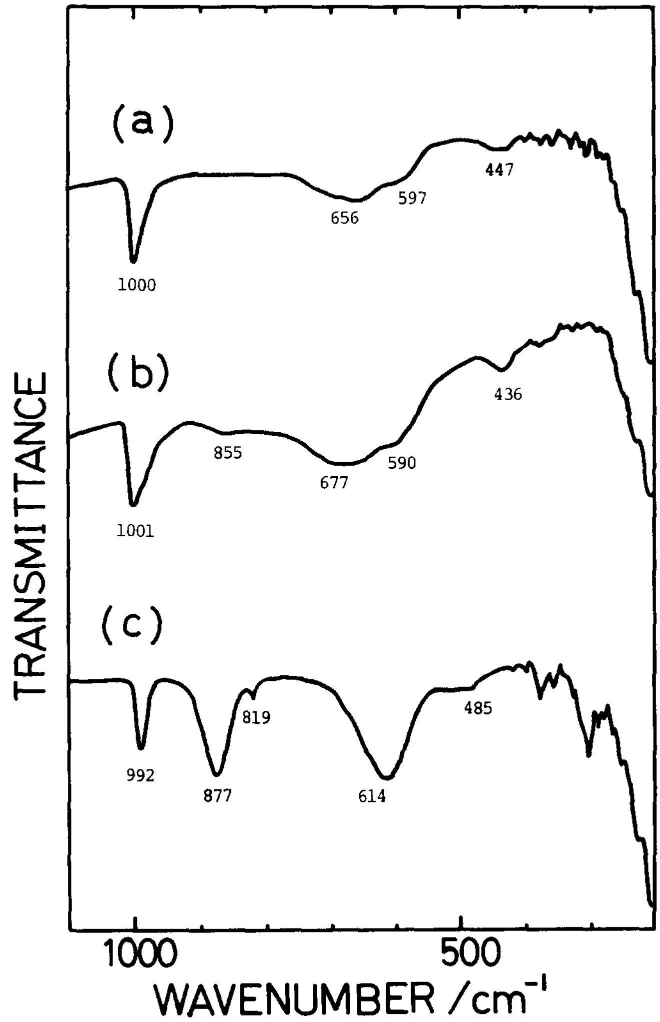

FIG. 3. IR spectra of (a) $H_{0.34}MoO_3$, (b) $H_{0.21}MoO_3$, and (c) MoO_3.

drogen contents, which were prepared by heating $H_{0.34}MoO_3$ *in vacuo*, have been studied by means of IR spectroscopy and X-ray diffraction. These results are given in Figs. 5 and 6. The IR results (Fig. 5) are in good agreement with those by Ohno *et al.* (*3*). With decreasing hydrogen content, new bands appeared at 983, 899, 863, 819, and 480 cm^{-1}, accompanied by the disappearance or reduction of the bands at 1000, 656, and 447 cm^{-1}. Thus, these changes might result from structural alterations described below rather than from the lowering of the conductivity. The X-ray diffraction results (Fig. 6) show that with decreasing hydrogen content the diffraction peaks of Type-I gradually change to a broad lineshape without the appearance of new diffraction peaks. It has been reported that Type-I is gradually decomposed by heating *in vacuo* to a nonstoichiometric compound with the rhombic MoO_3 structure (*5*), which produces diffraction peaks similar to those of Type-I. The broadening may be caused by

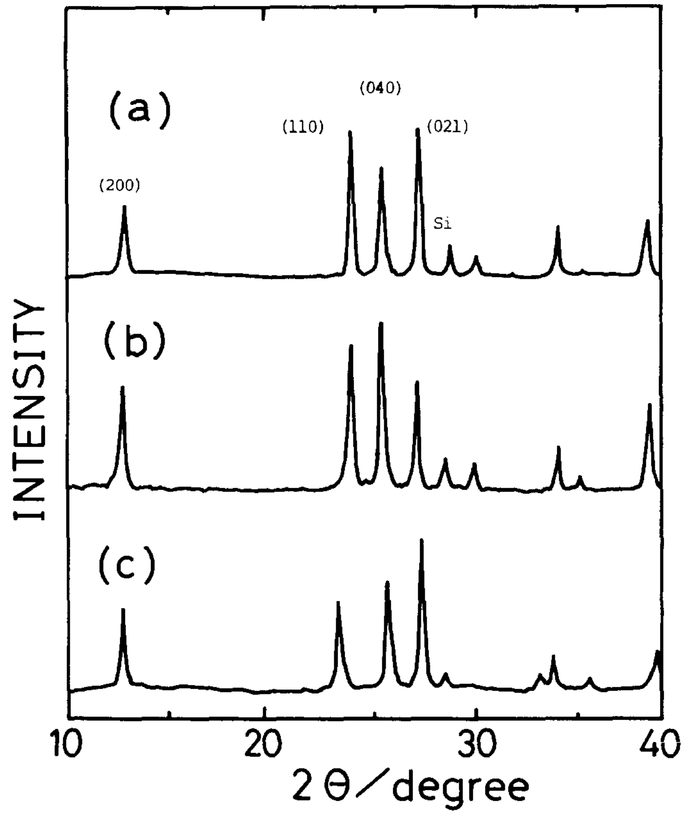

FIG. 4. Powder X-ray diffraction patterns of (a) $H_{0.34}MoO_3$, (b) $H_{0.21}MoO_3$, and (c) MoO_3.

the presence of a mixture of Type-I and MoO_3-like structures. The new bands at 983, 899, 863, 819, and 480 cm^{-1} in the IR spectra, which appear when samples are heated *in vacuo*, are similar to those of MoO_3 and can be attributed to the MoO_3-like structure. Figure 5 shows that both Type-I and MoO_3-like structures are present in all samples except $H_{0.34}MoO_3$. The samples with $x = 0.28$ and 0.18 contain MoO_3-like structures, although they produce only the X-ray diffraction pattern of Type-I. Figures 3 and 4 show that this is also the case for $H_{0.21}MoO_3$ and that in Type-I with a low hydrogen content a MoO_3-like configuration partly remains, even though this cannot be established by X-ray diffraction methods. Therefore, it can be claimed that the spectrum of $H_{0.34}MoO_3$ in the present work is the typical spectrum of Type-I. The band at 855 cm^{-1} of $H_{0.21}MoO_3$ and the above-mentioned extraneous bands in previous spectroscopic data (Table VI) are attributed to MoO_3-like structure or MoO_3.

Other Spectroscopic Data of Type-I

The author also has studied the Raman spectra of Type-I and has confirmed that there is no Raman band between 950 and 650 cm^{-1}. The result cannot be reported in detail in this paper, because much further effort is needed to clarify the problems of contamination with MoO_3 owing incomplete reactions in the preparation of sample and due to degradation by the laser. The confirmed results will be reported elsewhere.

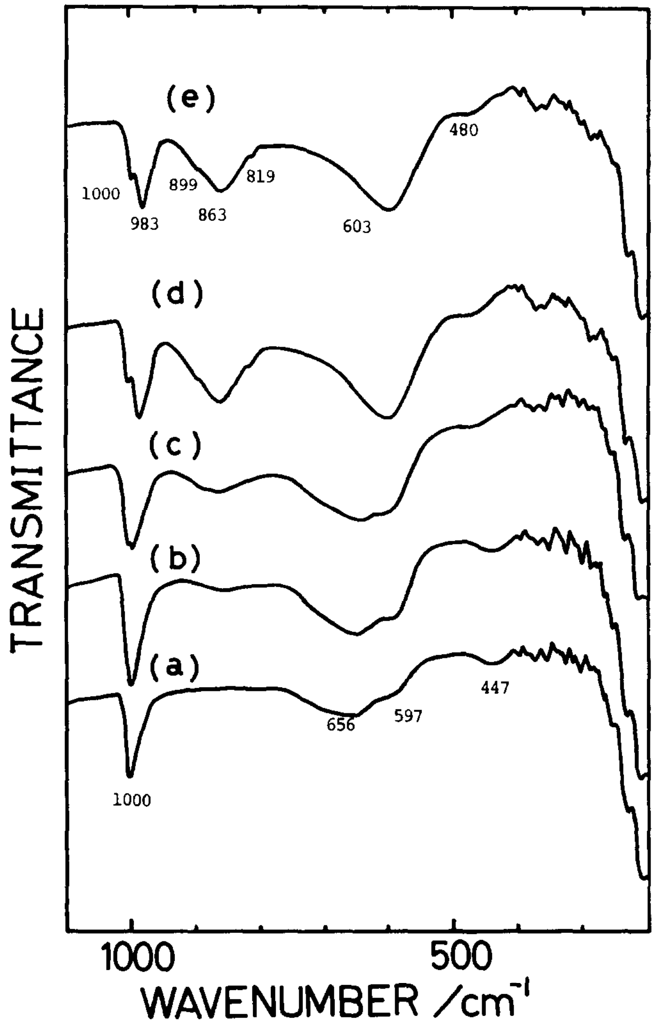

FIG. 5. IR spectra of (a) $H_{0.34}MoO_3$, (b) $H_{0.28}MoO_{2.97}$ (prepared by heating $H_{0.34}MoO_3$ *in vacuo* for 1 hr at 473 K), (c) $H_{0.18}MoO_{2.92}$ (at 573 K), (d) $MoO_{2.83}$ (at 673 K), and (e) $MoO_{2.83}$ (at 698 K).

Inelastic neutron scattering (INS) data were reported by Dickens *et al.* (*8*) who observed the band near 800 cm^{-1}. This is in conflict with the calculated and experimental results in this work. Further INS studies should be carried out.

Assignment of Observed Modes in IR Spectra

Type-I and MoO_3. The frequencies of the observed bands for $H_{0.34}MoO_3$ and MoO_3 are in good agreement with the calculated values, except for the band at 877 cm^{-1} for MoO_3 (Fig. 3 and Table III). These bands can be assigned by considering the calculated potential energy distributions. For MoO_3, the band at 992 cm^{-1} is assigned to Mo–O[1] stretching vibration, 819 cm^{-1} to Mo–O[3,3′]–Mo stretching, and 614 cm^{-1} to Mo–O[2′]–Mo stretching. For $H_{0.34}MoO_3$ the band at 1000 cm^{-1} is assigned to Mo–O[1] stretching vibration, 656 cm^{-1} to

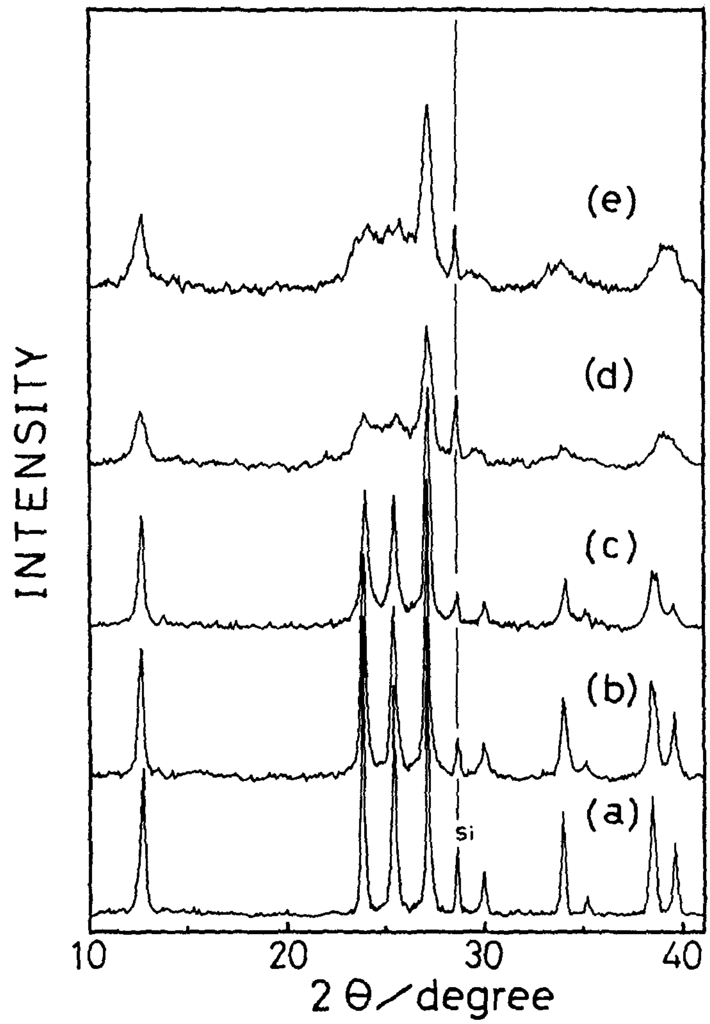

FIG. 6. Powder X-ray diffraction patterns of (a) $H_{0.34}MoO_3$, (b) $H_{0.28}MoO_{2.97}$, (c) $H_{0.18}MoO_{2.92}$, (d) $MoO_{2.83}$ (prepared at 673 K), and (e) $MoO_{2.83}$ (at 698 K).

Mo–O[3,3′]–Mo stretching, and 597 cm^{-1} to Mo–O[2′]–Mo stretching. The bands at 447 cm^{-1} for Type-I and at 470 cm^{-1} for MoO_3 are assigned to vibrational modes which have an important (ca. 40%) potential energy distribution to the Mo–O[2] stretching. The band at 877 cm^{-1} for MoO_3, which frequency does not agree with the calculated results, is assigned to another Mo–O[3,3′]–Mo stretching on the basis of the study by Py and Maschke (7). This assignment, which gives two bands for one calculated eigenmode, is not in conflict with the basis of this calculation. One calculated eigenmode corresponds to two fundamental vibrations, because the calculations have been carried out on one of two equivalent sheets in the unit cell by assuming that correlation field splitting effects are small, as mentioned above. Thus, the bands, except those at 877 and 819 cm^{-1}, may be twofold degenerate. The above assignment for $H_{0.34}MoO_3$ and MoO_3 is shown in Table V.

Mixture of Type-I and MoO_3-like structure. The bands of $H_{0.21}MoO_3$ and $MoO_{2.83}$ can be assigned by considering the corresponding specifications in $H_{0.34}MoO_3$ and MoO_3. The results are shown in Table V. For $MoO_{2.83}$ the three bands at 899, 863, and 819 cm^{-1} have been assigned to Mo–O[3,3′]–Mo stretching vibrations of MoO_3-like structure. This is in conflict with the number of eignmodes, but may be due to the distortion of structure in the mixture.

Changes in IR Spectra with Rearrangement of Mo–O

Type-I and MoO_3. As shown in Table V, when MoO_3 is transformed to Type-I, the band assigned to Mo–O[1] stretching vibration shifts to higher frequency by about 10 cm^{-1}, while the bands assigned to two Mo–O[3,3′]–Mo stretchings shift to lower frequency by about 220 cm^{-1} (from 877 to 656 cm^{-1}) and about 160 cm^{-1} (from 819 to 656 cm^{-1}); and the band assigned to Mo–O[2′]–Mo stretching is lowered by about 20 cm^{-1}. The changes in the bond lengths of Mo–O[3] and Mo–O[3′] may result in a shift from 819 to 656 cm^{-1} for Mo–O[3,3′]–Mo stretching, as shown by the calculated results.

$H_{0.34}MoO_3$ heated in vacuo. With the decrease in hydrogen content, successive spectral changes have been observed (Fig. 5). According to the assignment in Table V, the spectral changes of the region 1000–900 cm^{-1} in Fig. 5 result from situations of Mo–O[1] with alternation from Type-I to MoO_3-like structure; those in the region 900–650 cm^{-1} are linked to the structural change of Mo–O[3,3′]–Mo. This suggestion for the changes of the range 1000–900 cm^{-1} agrees with that of Ohno *et al.* (*3*). The changes of the region 900–650 cm^{-1} may be caused by the same change in the bond lengths of Mo–O[3] and Mo–O[3′], as in the case of MoO_3 and Type-I.

Deviation of Calculated Frequencies from Observations

As mentioned above, the band at 877 cm^{-1} of MoO_3 is not in agreement with the calculated results. It is well known (*19*) that vibrational frequencies observed in IR spectra do not necessarily represent fundamental vibrational frequencies, because of longitudinal–transverse splitting effects. The extent of these splitting effects cannot be estimated by the calculation in this work, which deals with factor group splitting effects or unit cell group splitting effects (*19*). The deviation for the band at 877 cm^{-1} may result from a large longitudinal–transverse splitting effect (*7*).

The proper calculation of the vibrational frequency change with the structural change between Type-I and MoO_3 has been achieved for the Mo–O[3,3′]–Mo stretching vibrations, except for the effect of longitudinal–transverse splitting. For the Mo–O[1] stretching vibrations, the spectral change has not been properly predicted; this change may be too small for the rough approximation procedure.

For a more exact treatment, it is necessary to extend the calculations to all sections in the unit cell by considering interlayer interactions and by using more suitable force constants (particularly angle-deformation force constants). Moreover, it is necessary to estimate the extents of longitudinal–transverse splitting for all vibrations, apart from such a calculation.

Recently Dickens *et al.* reported that they observed -OH group on Type-I by IR (*20*). This may suggest the need to consider H atoms as -OH. Further discussion on dealing with H atoms will be needed to obtain a more correct calculation, although the good agreement of the calculated results in the present work with experimental values indicates that influence of H atoms is not large.

Conclusion

The vibrational frequencies calculated by using the structural data for Type-I are in good agreement with IR spectroscopic data, although the calculation has been carried out by ignoring inserted hydrogen atoms. From these results it has been confirmed that previous spectroscopic data for Type-I involve the bands associated with the MoO_3-like structure. Appreciable differences between Type-I and MoO_3 have been observed in the region 900–650 cm^{-1} of IR spectra and have been explained as the result of a rearrangement of Mo–O[3,3′]–Mo in the Mo–O framework.

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