

Inelastic Neutron Scattering Spectrum and Normal Coordinate Analysis of the Insertion Compound $H_{1.7}MoO_3$

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High-resolution, incoherent inelastic neutron scattering (IINS) spectra have been recorded for the hydrogen insertion compound $H_{1.7}MoO_3$ and the related oxide hydrate $\alpha-MoO_3 \cdot H_2O$. Using the techniques of normal coordinate analysis, the normal modes of vibration of $H_{1.7}MoO_3$ have been calculated for a structure in which hydrogen is present in the form of $-OH_2$ groups. The results demonstrate that the measured IINS spectrum is consistent with this structural model and does not provide any support for alternative modes of attachment of hydrogen. The IINS spectrum and structural similarities of $\alpha-MoO_3 \cdot H_2O$ are discussed in light of these results. © 1994 Academic Press, Inc.

INTRODUCTION

Incoherent inelastic neutron scattering (IINS) (1) has proved to be a useful tool for the study of hydrogen insertion compounds of metal oxides. Investigation by optical spectroscopies is often precluded by the deep colors and metallic nature of such compounds. By contrast, as IINS spectra are dominated by modes involving large amplitudes of vibration of light atoms with large incoherent scattering cross sections, the spectra are dominated by hydrogenic vibrations. Qualitative analysis of spectra has yielded useful information for a number of insertion compounds (2, 3). More recently we have attempted to place the analysis on a more quantitative basis using the techniques of normal coordinate analysis (NCA) (4). In this work we present such a study on the insertion compound $H_{1.7}MoO_3$.

Ambient temperature reduction of molybdenum trioxide may be accomplished either chemically with nascent hydrogen or electrochemically in acidic media to yield compounds of the form H_xMoO_3 ($0 \leq x \leq 2.0$) (5). Three, variable-composition, nonstoichiometric phases have been reported with nominal compositions $H_{0.4}MoO_3$, $H_{1.0}MoO_3$, and $H_{1.7}MoO_3$, together with a line phase $H_{2.0}MoO_3$ (6). The structures of these compounds appear,

on the basis of powder X-ray diffraction data, to be closely related to that of MoO_3 itself, which adopts a unique layer structure in which zigzag chains of edge-sharing octahedra are joined by sharing corners. Figure 1 shows the idealized arrangement, whereas in practice the octahedral coordination about Mo is considerably distorted. The insertion compounds are highly colored, the color depending on the degree of reduction, and have electronic properties ranging from semiconducting to metallic. The properties of these materials have been investigated extensively (7).

Elastic and inelastic neutron scattering studies on $H_{0.34}MoO_3$ have demonstrated (8) that the inserted hydrogen atoms are located within MoO_3 layers attached to bridging oxygen (O2) atoms in the form of $-OH$ groups. These conclusions have been further supported by NMR evidence (9), and more recently Eda (10) has presented optical spectroscopic data which support this structural picture.

The site of attachment of hydrogen in the phase of nominal composition $H_{1.7}MoO_3$ is the subject of greater debate. On the basis of qualitative analysis of the IINS spectrum of $H_{1.68}MoO_3$ it was suggested (8) that the inserted hydrogen was present in the form of $-OH_2$ groups. A recent structural study by powder neutron diffraction on the deuterated analogue (11) located the hydrogen in sites about the terminal oxygen (O3) with a corresponding increase in the length of the Mo–O3 bond. Partial occupancy of the four sites around each O3, such that each of the $-OH$ bonds is directed at a terminal oxygen in the adjacent layer, corresponds to the presence of $-OH_2$ groups in the interlayer space. These $-OH_2$ groups are oriented in one of two mutually perpendicular directions. The proposed structure would appear to have structural features in common with the white form of molybdic acid, $\alpha-MoO_3 \cdot H_2O$, the structure of which consists of isolated double chains of MoO_6 octahedra with each molybdenum bearing an $-OH_2$ group protruding between the chains (Fig. 2).

The structural picture for $H_{1.7}MoO_3$ is further complicated by several NMR studies which have been performed on both $H_{1.7}MoO_3$ and $D_{1.7}MoO_3$. Different workers have

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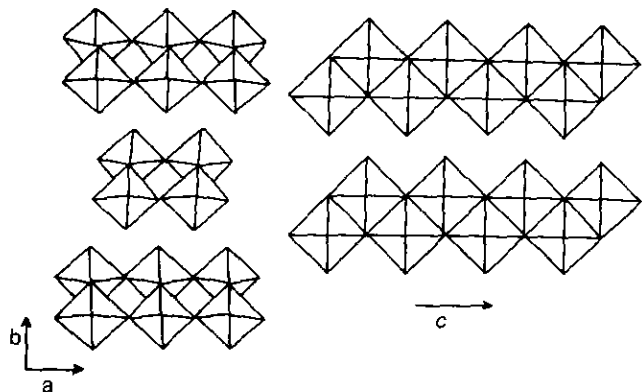


FIG. 1. Idealized structure of MoO_3 consisting of vertex- and edge-linked MoO_6 octahedra.

reached contradictory and conflicting conclusions regarding the placement of hydrogen. Alternative models proposed range from those which require the presence of two distinct $-\text{OH}$ (12) groups to those involving a combination of $-\text{OH}$ and $\text{Mo}-\text{H}$ groups (13). In order to investigate further the mode of hydrogen attachment in $\text{H}_{1.7}\text{MoO}_3$, a new high-resolution IINS spectrum is presented and discussed here. An attempt is then made to rationalize the spectrum by utilizing available crystallographic information to perform a NCA. In order to use as self-consistent a set of force constants as possible, the bond-stretching force constants were calculated according to the empirical relationship of Cotton and Wing (14). A number of alternative sets of force constants have been utilized for MoO_3 by other workers, and their use is discussed here. In addition, an IINS spectrum has been recorded for $\alpha\text{-MoO}_3 \cdot \text{H}_2\text{O}$ and is discussed in the light of the NCA performed on $\text{H}_{1.7}\text{MoO}_3$.

EXPERIMENTAL

$\text{H}_{1.7}\text{MoO}_3$ was prepared according to the method of Birtill and Dickens (5) by prolonged reaction of zinc and 6 M HCl with a slurry of MoO_3 under a nitrogen atmosphere. Following washing and drying, the green product ($\text{H}_{2.0}\text{MoO}_3$) was dehydrogenated by heating at 110°C for 12 hr under a reduced pressure of 10^{-2} Torr. The resulting red powder was then removed to an argon atmosphere dry box. Reducing power analysis by the method of Choain and Marion (15) confirmed the composition to be $\text{H}_{1.7}\text{MoO}_3$. Powder X-ray diffraction data showed the compound to have a monoclinic unit cell with lattice parameters in agreement with those reported previously (5).

$\alpha\text{-MoO}_3 \cdot \text{H}_2\text{O}$ was prepared from the dihydrate $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ by a modification of the method previously reported by Freedman (16). Yellow $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ was synthesized by acidification of a solution of sodium molyb-

date. Five grams of the dihydrate was then sealed into a Parr acid digestion bomb with 30 cm^3 of 5 M HCl, and the mixture was warmed at 45°C for four days. The resulting white solid was centrifuged and washed with distilled water prior to drying in air. Powder X-ray diffraction data were in agreement with those reported previously (17). Thermogravimetric analysis gave the composition as $\text{MoO}_3 \cdot 0.98\text{H}_2\text{O}$.

IINS spectra were recorded at 20 K on the time focused crystal analyzer (TFXA) spectrometer on the ISIS spallation source, Rutherford Appleton Laboratory. Samples were loaded into thin-walled aluminum sachets under an atmosphere of dry argon. The sachets were then sealed by crimping their ends and stored under argon prior to mounting on a standard sample stick in a closed cycle refrigerator (CCR). Spectra were recorded over the complete energy range of the instrument ($20\text{--}4000\text{ cm}^{-1}$). Details of the spectrometer have been given elsewhere (18).

CALCULATION OF THE VIBRATIONAL MODES OF $\text{H}_{1.7}\text{MoO}_3$

Normal modes of vibration were calculated by means of the GF matrix method using the SOTONVIB program previously described by Beattie *et al.* (19). The unit cell of the proposed structure of $\text{H}_{1.7}\text{MoO}_3$ contains four formula units in two layers. The complexity of the calculation of normal modes increases rapidly as the number of atoms increases. For this reason, only a single layer of the structure was considered in this work. This approximation has previously been used successfully by Beattie *et al.* in their treatment of MoO_3 . More recent work by Py and Maschke (20) provides support for this single-layer approximation. Their calculations on a chain, single layer, and full crystal lattice of MoO_3 demonstrated that the interactions vary in the order intrachain $>$ interchain \gg interlayer. Coupling

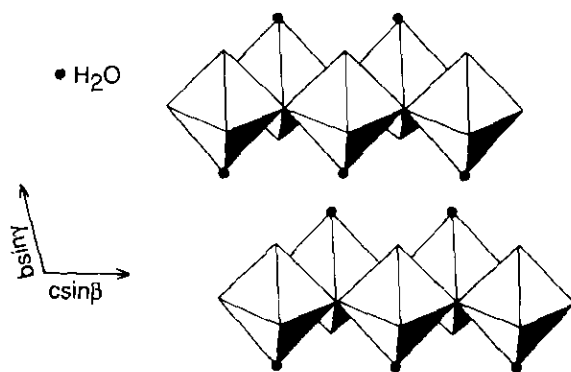


FIG. 2. Idealized structure of $\alpha\text{-MoO}_3 \cdot \text{H}_2\text{O}$ showing the presence of $-\text{OH}_2$ groups between the layers of MoO_6 octahedra, similar to those in $\text{H}_{1.7}\text{MoO}_3$.

TABLE 1
Force Constants Used in the Calculation of Normal Modes of MoO_3

Bond stretch	Bond length (Å)	k (mdyn Å ⁻¹)
Mo-O3	1.67	7.8
Mo-O1	1.95	2.95
Mo-O2	1.73	6.20
Mo-O2	2.25	1.30
Mo-O1	2.33	1.0
Angle deformation	Bond lengths (Å)	k (mdyn Å rad ⁻²)
O2-Mo-O3	1.67/1.73	1.1
O2-Mo-O3	1.67/2.25	0.4
O1-Mo-O3	1.67/1.95	0.8
O1-Mo-O2	1.95/1.73	0.55
O1-Mo-O1	1.95/2.25	0.2
O1-Mo-O2	1.73/2.33	0.3
O1-Mo-O2	2.25/2.33	0.15
Mo-O-Mo ^a		0.3

^a All motions in which oxygen is the central atom.

between layers was found to perturb significantly only the very low frequency modes.

Force constants, covering the range of bond lengths relevant to this work, were taken from the plot of Cotton and Wing (14) and replotted as k versus r^{-6} . Simple interpolation from the resulting linear plot permitted calculation of force constants for any given bond length. Angle bending force constants were derived from previous work on oxide phonon spectra (21). In order to assess the validity of the r^{-6} functional dependence of the stretching force constants the calculation of Beattie *et al.* for MoO_3 was repeated. A simple valence force field,

$$2V = \sum_i k_r \Delta r_i^2 + \sum_j k_\theta \Delta \theta_j^2,$$

involving bond stretches Δr_i and angle deformations $\Delta \theta_j$ was used. All input to the program, with the exception of the stretching force constants, which were calculated by reference to the aforementioned plot, was as described in the original paper of Beattie *et al.* Force constants used in this calculation are set out in Table 1. A single layer of MoO_3 contains two formula units and adopts the space group $P2_1/m$. The 21 optic modes which span an irreducible representation

$$\Gamma_{opt} = 8A_g + 4B_g + 3A_u + 6B_u$$

are given in Table 2 together with experimental data. Examination of the eigenvectors of the normal modes allows assignment of these vibrations in terms of bond-stretching and angle deformation motions. Overall

agreement is comparable with that achieved by Beattie *et al.*, and the assignments are in agreement with those of Mattes and Schroder (22). The notable exception is the stretching frequency of the 3-connected oxygen (O1). The components of this have been observed at 545 and 668 cm^{-1} , whereas they are calculated here at 836 and 833 cm^{-1} . In an attempt to improve the agreement between the observed and the calculated frequencies, alternative sets of bond-stretching force constants were considered. Kharitonov and Gerzha (23) have proposed two formulae for the calculation of bond-stretching force constants for bond lengths in the ranges $1.63 \leq r(Mo-O) \leq 1.88$ and $1.88 \leq r(Mo-O) \leq 2.3$. Applying these formulae to the case of MoO_3 gives rise to the set of stretching force constants shown in Table 3. It can be seen that these values are somewhat larger than those derived from the plot of Cotton and Wing and therefore give rise to higher calculated frequencies in the bond-stretching region. By contrast the set of force constants given by Py and Maschke (Table 3) results in a considerable improvement in the agreement over the entire spectral range. However, these force constants, which were obtained by least-squares minimization, do not have any simple functional dependence on bond length. Therefore, although this set of force constants results in an improved agreement between observed and calculated data, they do not provide a rational means of obtaining interpolated values which may be applied to $H_{1.7}MoO_3$. It is the hydrogenic modes of $H_{1.7}MoO_3$ that are the chief concern of this work. In the absence of vibrational spectroscopic data for the metal-oxygen framework of $H_{1.7}MoO_3$, only indirect information is available for those metal-oxygen stretching vibrations which have appreciable hydrogenic components. For these reasons, the relationship of Cotton and Wing was utilized in calculating a self-consistent set of force constants for the NCA of $H_{1.7}MoO_3$.

As the SOTONVIB program has no facility for allowing

TABLE 2
Observed and Calculated Frequency Data for MoO_3

Observed frequency (cm^{-1})	Calculated frequency (cm^{-1})	Assignment	Symmetry
1004, 997	994, 993	$\nu(Mo-O3)$	B_u, A_g
820, 840	957, 957	$\nu(Mo-O2)$	A_g, B_u
648, 646	836, 833	$\nu(Mo-O1)$	A_u, B_g
505, 473	534, 500	$\nu(Mo-O1)$	B_u, A_g
382, 371	374, 366	$\delta(O2-Mo-O3)$	A_g, B_u
351, 340	294, 282	$\delta(O1-Mo-O2)$	B_u, A_g
265, 259	266, 261	$\delta(O3-Mo-O1)$	B_g, A_u
219, 202	223, 205	$\delta(O2-Mo-O3)$	A_g, B_u
218, 217	218, 217	$\delta(O1-Mo-O2)$	B_g, A_u
160, 118, 84	160, 84, 57	Mixed modes	A_g, B_g, A_g

TABLE 3
Alternative Bond-Stretching Force Constants and Resulting
Frequencies for MoO₃

Bond length (Å)	Bond-stretching force constants		
	Cotton and Wing (14)	Py and Maschke (20)	Kharitonov and Gerzha (23)
1.67	7.80	7.92	8.07
1.95	2.95	1.73	3.12
1.73	6.20	4.66	6.80
2.25	1.30	0.80	1.53
2.33	1.0	0.8	1.26

Mode	Frequency (cm ⁻¹)		
$\nu(\text{Mo-O3})$	994, 993	996, 995	1024, 1023
$\nu(\text{Mo-O2})$	957, 957	822, 822	996, 995
$\nu(\text{Mo-O1})$	836, 833	650, 653	872, 874
$\nu(\text{Mo-O1})$	534, 500	486, 454	567, 531

partial occupancy of atomic sites, the simulation was performed for the stoichiometric composition H_{2.0}MoO₃. The fractional atomic coordinates for the monoclinic unit cell determined by powder neutron diffraction were transformed to an orthogonal axial system. The Cartesian coordinates of the 20 atoms required to define 62 internal coordinates are given in Table 4, while Fig. 3 illustrates the structure of the single layer considered and defines the numbering scheme adopted for the atoms.² The unit cell of a single layer has a space group *P2/m* and contains two H_{2.0}MoO₃ formula units. The 33 normal modes span an irreducible representation.

$$\Gamma_{\text{opt}} = 15A_g + 6A_u + 3B_g + 9B_u.$$

Powder neutron diffraction on H_{1.68}MoO₃ indicates that insertion of hydrogen results in a more regular coordination geometry about Mo than is found in the parent oxide. The smaller range of Mo-O bond lengths gives rise to much less variation in the bond-stretching force constants calculated from the r^{-6} relationship (Table 5). In addition, the more regular geometry led us to adopt a reduced number of angle bending force constants. The simple valence force field was modified by the addition of terms arising both from torsional motions of the -OH₂ group about the Mo-O3 bond and from movement of one hydrogen atom of a pair out of a plane defined by its partner

² The complete input file for this calculation together with the output files generated may be obtained on request to the authors.

TABLE 4
Cartesian Coordinates Required to Define the Internal
Coordinates Used in NCA Calculation for H_{1.7}MoO₃

Atom number	Atom type	X (Å)	Y (Å)	Z (Å)
1	Mo	0.9403	0.0	0.8045
2	Mo	-0.9403	0.0	3.2545
3	O1	1.0371	0.0	2.8640
4	O1'	-1.0371	0.0	1.1950
5	O2	1.0647	1.8865	0.8407
6	O2'	-1.0647	-1.8865	3.2183
7	O3	3.1113	0.0	0.7905
8	O3'	-3.1113	0.0	3.2685
9	H1	3.6229	-0.5810	0.1549
10	H2	3.6506	0.5697	1.3301
11	H1'	-3.6229	-0.5810	3.9041
12	H2'	-3.6506	0.5697	2.7289
13	Mo(T) ^a	0.9403	0.0	4.8635
14	Mo(T)	-0.9403	0.0	-0.8045
15	Mo(T)	0.9403	3.7730	0.8045
16	Mo(T)	-0.9403	-3.7730	3.2545
17	O1(T)	1.0371	0.0	-1.1950
18	O1'(T)	-1.0371	0.0	5.2540
19	O2(T)	1.0647	-1.8865	0.8407
20	O2'(T)	-1.0647	1.8865	3.2183

^a T denotes an atom translationally related to one in the unit cell.

and two oxygen atoms. This force field contained squared terms only.

RESULTS AND DISCUSSION

The IINS spectrum of H_{1.7}MoO₃ which is shown in Fig. 4 is similar in general appearance to that reported previously (8). However, the higher resolution of TFXA results in more detail being apparent, particularly in the 300-500 and 600-1100 cm⁻¹ regions. Of the 33 frequencies

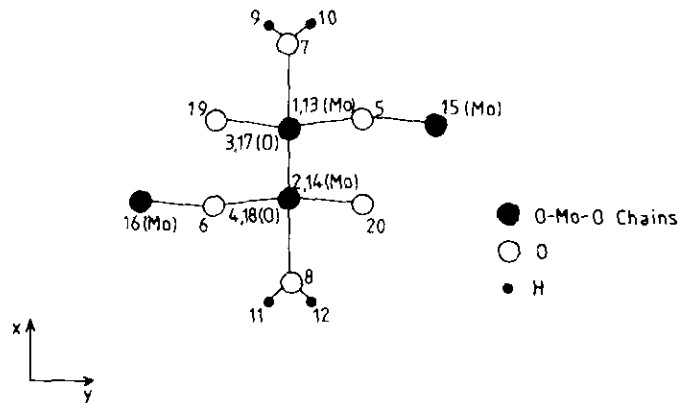


FIG. 3. The single layer of H_{1.7}MoO₃ used in the calculation of the normal modes. The numbers in the figure refer to the atom numbers in Table 4.

TABLE 5
Force Constants Used in Calculation of Normal Modes
of $H_{1.7}MoO_3$

Bond stretch	Bond length (Å)	k (mdyn Å ⁻¹)
Mo-O1	2.06	2.2
Mo-O1	2.00	2.65
Mo-O1	2.02	2.45
Mo-O2	1.89	3.70
Mo-O3	2.17	1.6
O3-H	1.0, 0.95	6.8
Angle deformation	Bond lengths (Å)	k (mdyn Å rad ⁻²)
O3-Mo-O2	2.17/1.89	0.3
O3-Mo-O1	2.17/2.06	0.3
O3-Mo-O1	2.17/2.00	0.3
O2-Mo-O1	1.89/2.06	0.2
O2-Mo-O1	1.89/2.00	0.2
O2-Mo-O1	1.89/2.02	0.2
O1-Mo-O1	2.06/2.02	0.2
O1-Mo-O1	2.0/2.02	0.2
Mo-O-Mo ^a		0.3
H-O3-Mo		0.48
H1-O3-H2		0.45
-OH ₂ torsion		0.05
Out-of-plane motion of H		0.16

^a All motions in which oxygen is the central atom.

calculated for $H_{1.7}MoO_3$, by normal coordinate analysis, only those with appreciable hydrogenic components to their eigenvectors are tabulated together with observed frequencies and assignments in Table 6. All assignments were arrived at by careful examination of the corresponding eigenvectors together with an analysis of the potential energy distribution among the force constants. There is good agreement between observed and calculated data. The most intense peaks at 979 and 883 cm^{-1} may be assigned, respectively, to rocking and wagging vibrations of the $-OH_2$ group. It is notable that these values are in the upper range of the spectral region for which these librational modes have been observed in the infrared spectra of a range of hydrates. The spectral resolution in this region is not sufficient to identify a feature corresponding to the mixed mode calculated at 954 cm^{-1} . NCA allows unambiguous assignment of the modes at 461 and 400 cm^{-1} to a torsional mode and a Mo-OH₂ stretching fundamental, respectively. The latter is observed in the IINS spectrum as the oxygen (O3) "carries" two hydrogen atoms as it vibrates, a view confirmed by examination of the eigenvectors. The low-frequency mode at 180 cm^{-1} is similar to that observed in the IINS spectra of other hydrogen insertion compounds and arises from an activation of the density of states of the oxide lattice (2). The feature observed at 1652 cm^{-1} is characteristic of a scis-

sors vibration of an $-OH_2$ group; this is borne out by examination of the corresponding eigenvectors. Schematic representations of the hydrogenic modes are given in Fig. 5.

Adoption of a self-consistent set of bond-stretching force constants based on an r^{-6} dependence has allowed us to calculate for the hydrogen motions, normal modes for the crystallographic structure which are in reasonable agreement with those observed by IINS. The adoption of a force constant which produces an anomalously high calculated frequency for the Mo-O1 stretching fundamental of MoO_3 does not appear to have affected this agreement adversely. While anomalies such as this may be corrected, given appropriate experimental data, by suitable adjustment of force constants, their root is more likely to lie in the choice of force field. For example, Eda (10), in recent work on $H_{0.34}MoO_3$ utilizing slightly modified bond-stretching force constants of Py and Maschke together with the angle bending force constants of Beattie *et al.*, achieved reasonable agreement with infrared and Raman data. However, comparison with previously reported IINS data reveals a discrepancy for the stretching mode of the bridging oxygen to which the inserted hydrogen is attached. There is a certain arbitrariness in the choice of a particular set of force constants, the inability to fit the entire spectral region with a single set lying in the use of a SVFF. A more generalized force field allowing interactions between the various modes has been found in similar cases to improve the fit (24). However, the more general the force field becomes, the less easily identified are the terms which it contains. It was our intention in this work to investigate whether the observed IINS spectrum was compatible with the structural model proposed from powder neutron diffraction while utilizing a force field which could be described in terms of physically meaningful parameters. Given the restrictions of using a SVFF the agreement is remarkably good. However, it is desirable to consider whether the experimental data can be accounted for by any of the other structural

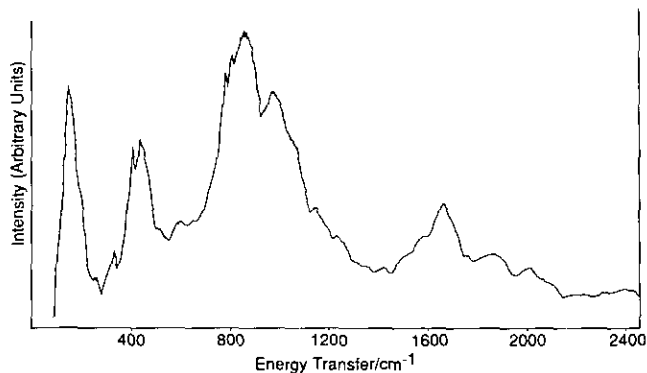


FIG. 4. IINS spectrum of $H_{1.7}MoO_3$ recorded at 20 K.

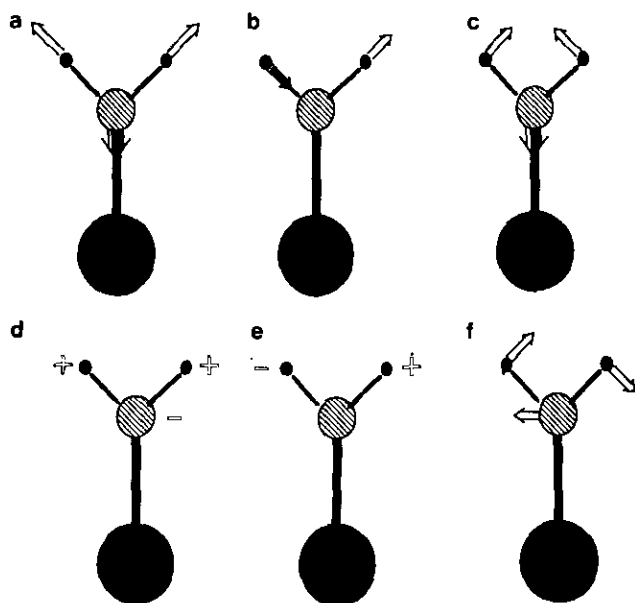


FIG. 5. Schematic representation of the vibrational modes of the $-\text{OH}_2$ group in $\text{H}_{1.7}\text{MoO}_3$. The large filled circles represent molybdenum, the smaller hatched circles oxygen, and the small solid circles hydrogen. Arrows represent approximate relative displacements in the plane of the page, and $+/-$ signs indicate displacements perpendicular to this plane. (a), (b), and (c) are external modes, and (d), (e), and (f) are internal (librational) modes (wagging, torsional, and rocking, respectively).

models proposed. A feature of a number of the alternative structural models is the hydride-like appearance of the NMR spectra. Various workers have suggested that this is due to some or all of the hydrogen being present in the form of $\text{MO}-\text{H}$ groups. However, vibrational studies on a number of transition metal hydrido complexes (25) reveal a characteristic frequency for the $\delta(\text{M}-\text{H})$ mode in the $600-800\text{ cm}^{-1}$ region. The IINS spectrum presented here does not contain any significant features in this region, casting doubt on the presence of such a unit. The suggestion that $\text{H}_{1.7}\text{MoO}_3$ contains two separate $-\text{OH}$ groups has also been made. However, a NCA performed on $\text{H}_{0.34}\text{MoO}_3$ (26), which contains a single $-\text{OH}$ group, yields, assuming an r^{-6} dependence to the stretching force constants, calculated frequencies for the bending vibrations of the $\text{Mo}-\text{OH}$ unit of 1309 and 650 cm^{-1} . These compare with values of 1267 and 517 cm^{-1} observed by IINS. Independent NMR investigations (9, 12) of $\text{H}_{1.7}\text{MoO}_3$ indicate that the structural picture may be more complicated than that of a simple hydrate. In particular, absorption spectra in the temperature range $77\text{ K} \leq T \leq 450\text{ K}$ suggest that a fraction of the hydrogen may be attached in the form of $-\text{OH}$ groups. Estimation of the areas under the absorption curve gave an estimate of 10% for this fraction. Although it would be anticipated that this fraction would give rise to features in the IINS spectrum

similar to those observed for $\text{H}_{0.34}\text{MoO}_3$, these would be very weak owing to the relatively small amount of hydrogen, corresponding to an approximate composition of $\text{H}_{0.17}\text{MoO}_3$, attached in this way. The high background in these spectral regions may well mask such features. For these reasons, although our data are interpretable in terms of a structural model involving $-\text{OH}_2$ groups alone, we cannot rule out the possibility of some of the attached hydrogen being present as hydroxyl groups. In order to investigate this possibility further it would be necessary to make use of a profile-fitting method in which intensities of each normal mode are considered in addition to their frequencies. For an extended solid of the complexity of $\text{H}_{1.7}\text{MoO}_3$ this is not currently practicable.

The IINS spectrum of $\alpha\text{-MoO}_3 \cdot \text{H}_2\text{O}$ (Fig. 6) is somewhat different in appearance, the bands being considerably sharper than those observed for $\text{H}_{1.7}\text{MoO}_3$. This may be indicative of substantial disorder in the latter compound. Boschen (27) has carried out extensive Raman and infrared investigations on $\alpha\text{-MoO}_3 \cdot \text{H}_2\text{O}$, and certain correlations may be drawn between the optical data and the IINS data presented here. The weak feature at 1657 cm^{-1} compares well with a value of 1638 cm^{-1} observed in the infrared and assigned by Boschen to the scissors vibration of the $-\text{OH}_2$ group. By analogy with $\text{H}_{1.7}\text{MoO}_3$, the peak at 370 cm^{-1} is in the spectral region expected for torsional oscillations/stretching vibrations of the $\text{Mo}-\text{OH}_2$ bond and, although not unambiguously assigned, compares with a value of 375 cm^{-1} observed by infrared. The strong features in the IINS at 630 and 567 cm^{-1} have no optical analogues. However, by analogy with other hydrates they would appear to arise from librational modes of the $-\text{OH}_2$ group. These values lie well

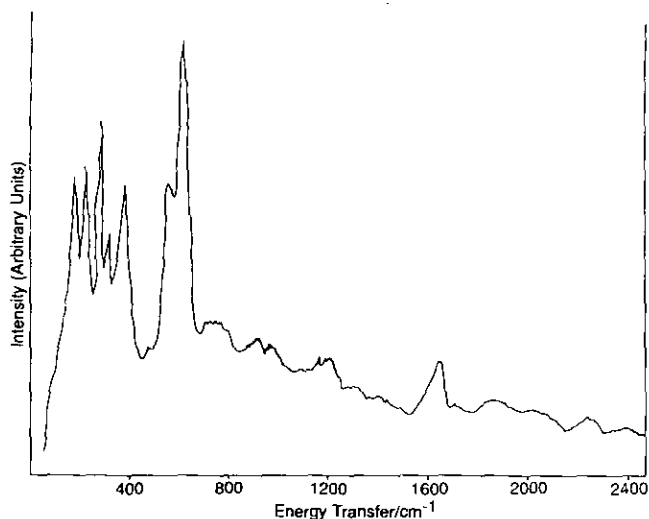


FIG. 6. IINS spectrum of $\alpha\text{-MoO}_3 \cdot \text{H}_2\text{O}$ recorded at 20 K .

TABLE 6
Observed and Calculated Frequency Data for $H_{1.7}MoO_3$

Calculated frequency (cm ⁻¹)	Observed frequency (cm ⁻¹)	Assignment	Symmetry
3547, 3547		$\nu(O-H)$	A_g, A_u
3462, 3462		$\nu(O-H)$	A_g, A_u
1659, 1659	1652	$\delta(H-O-H)$	A_g, A_u
979, 979	979	$\rho_{rock}(-OH_2)$	A_g, B_u
954, 954	979	$\rho_{rock}(-OH_2)/\nu(Mo-O_3)$	A_g, B_u
891, 891	883	$\rho_{wag}(-OH_2)$	A_g, B_u
464, 464	461	$\rho_{torsion}(-OH_2)$	A_g, B_u
429, 415	400	$\nu(Mo-O_3H_2)$	A_g, B_u

within the range 300–1000 cm⁻¹ quoted by Lutz (28) for a range of hydrates. This contrasts with $H_{1.7}MoO_3$, where the calculated (and observed) rocking and wagging vibrations of the $-OH_2$ unit are at the upper spectral range for these modes. It has been shown in the case of certain hydrates (25) that the librational frequencies of a bonded water molecule (to which the $-OH_2$ group in $H_{1.7}MoO_3$ is a good approximation) increase as the metal–oxygen (Mo–OH₂) interaction increases. The strength and hence length of the Mo–OH₂ bond is an indicator of the extent of this interaction. In $H_{1.7}MoO_3$ it is 2.17 Å, whereas in $\alpha-MoO_3 \cdot H_2O$ it is lengthened considerably to 2.35 Å. It has also been argued (29) that increased hydrogen bonding increases librational frequencies. In $H_{1.7}MoO_3$ this H-bonded distance is calculated as 1.98 Å. Although $\alpha-MoO_3 \cdot H_2O$ is known to be linked by a hydrogen-bonded network, the lack of knowledge of the hydrogen atom positions prevents calculation of an accurate length for the hydrogen bond. However, a reliable estimate of ~1.9 Å may be made based on the known Mo/O positions and a 1-Å O–H bond. The small differences in these values would lead us to expect similar librational frequencies in both $H_{1.7}MoO_3$ and $\alpha-MoO_3 \cdot H_2O$. Hence it is likely that it is the stronger Mo–OH₂ interaction in $H_{1.7}MoO_3$ that is the major factor in raising the librational frequencies in the latter.

CONCLUSIONS

Although the choice of force constants does provide some difficulties in a study such as this, we have demonstrated that it is possible to quantify the analysis of IINS spectra of hydrogen-containing systems by using the techniques of NCA. Such an analysis is greatly facilitated by

the fact that the IINS spectrum is dominated by those modes involving large amplitudes of vibration of hydrogen and that these modes are readily identified from an examination of the corresponding eigenvectors. In the system under investigation, analysis shows that the measured IINS spectrum is consistent with the crystallographically determined structure and would not arise from hydride-like species. Although the hydrogenic modes show strong similarities to those of bonded water molecules in metal salt hydrates, the possibility of the coexistence of $-OH$ and $-OH_2$ groups cannot be ruled out.

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