more favorable energetically. These considerations suggest that for the metal surface–alkyne reaction the basic driving force should be the same, i.e., negative charge transfer to the hydrocarbon. As the transition metals commonly used have lower electronegativities than carbon, this seems quite reasonable.

If the correlation with increasing charge does carry over to metal systems, then there should be a correlation between the ease of carbyne formation and the ease of charge transfer, i.e., the difference in electronegativities of the metal and carbon. For a given metal, C_2H_2 reacts more readily than C_2H_4 to form surface CH species.[50] This is consistent with our thesis as sp-hybridized carbon is more electronegative than sp^2-hybridized carbon. The irreversible chemisorption of hydrocarbons on various supported metals leads to residues with H/C ratios close to 1. The percent retention of a hydrocarbon as well as the fraction of surface covered by irreversible adsorbed species decreases as one moves from the iron group to the nickel group,[51] again correlating well with the change in electronegativity of the metal.

Although the description of carbyne formation driven by charge transfer is consistent with chemical intuition, charge flow in exactly the opposite direction of adsorption has been postulated previously.[52] On the basis of the negative change in metal work function following chemisorption of alkenes and alkynes, the suggestion has been made that the coordinated hydrocarbon has more positive ion character than negative character. There is no simple and pictorial MO theory for metals, and it is unlikely that a change in work function is simply connected to adsorbate charge. Even in our simple B_4C_2 model with well-defined MO's the lowest ionization potential varies unpredictably across the series and does not correlate with charge.[53]

There have been many approaches to the calculation of adsorption energies of which bond energy partitioning methods are one, e.g., the crystal field–surface orbital–bond energy bond order method.[55] The energetics of the series in Figure 1 tests the appropriateness of such an approach for a surface species. Figure 5 demonstrates a fairly linear correlation between the Mulliken overlap and the total BC interaction energy. The largest deviation from the curve is for **7** where the BC energy is underestimated. Note that in going from **6** to **7**, the B_4 "butterfly" structure is lost. We suggest, then, that as long as there are no large disruptions of the metal surface structure caused by the admolecule, the various energy partitioning methods are valid even if crude. Thus, the structures of the metal analogues of the compounds in Figure 1 may be used to gain insight into surface reaction energies for unsaturated hydrocarbons. The potential usefulness of such an approach depends on the characterization of more metal analogues of heteroboranes as well as the generation of suitable metal–carbon interaction energies.

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Registry No. **1a**, 74-85-1; **1b**, 18283-93-7; **2a**, 74-86-2; **3**, 36427-42-6; **4**, 79534-15-9; **5**, 18972-20-8; **6**, 20693-68-9; **7**, 20693-67-8.

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Contribution from the Laboratoire de Chimie des Métaux de Transition (ERA 07 0608),
Université Pierre et Marie Curie, 75230 Paris Cedex 05, France,
and the Laboratoire de Spectroscopie Infrarouge (LA 04 0124), Université de Bordeaux I, 33405 Talence Cedex, France

Vibrational Investigations of Polyoxometalates. 1. Valence Force Field of $Mo_6O_{19}^{2-}$ Based on Total Isotopic Substitution (^{18}O, ^{92}Mo, ^{100}Mo)

CLAUDE ROCCHICCIOLI-DELTCHEFF,*[1a] RENÉ THOUVENOT,[1a] and MONIQUE FOUASSIER[1b]

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A normal-coordinate treatment of the hexamolybdate anion $Mo_6O_{19}^{2-}$ was performed by using an internal valence force field. Total isotopic substitution (^{18}O, ^{92}Mo, ^{100}Mo) allowed previous erroneous assignments to be corrected. A reasonable force field accounting for the experimental data of the four isotopic derivatives is proposed. The principal force constants are discussed in relation with the geometry of the anion. In particular, the stretching force constants k_t (7.46 mdyn Å^{-1}), k_b (2.35 mdyn Å^{-1}), and k_c (0.47 mdyn Å^{-1}), respectively, agree with double bonds Mo–O_t, single bonds Mo–O_b, and very loose Mo–O_c bonds.

Introduction

Polyoxometalates are of great interest to workers in various fields of chemistry (e.g., ionic conductivity, photoconductivity, electronic hopping, catalysis, etc.). Their reactivity with other compounds, in particular with organometallic subunits, is widely studied. Moreover they can be considered as simplified models of three-dimensional frameworks. A good knowledge of their structural properties is required for a better understanding of the observed phenomena: the vibrational techniques can be suitable for this purpose. However, the assignments of IR and Raman spectra of such large polynuclear complexes are difficult and should be followed by a normal-coordinate analysis. Only a few attempts have been made up to now, probably because of the complexity of the theoretical treatment.

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(1) (a) Université Pierre et Marie Curie. (b) Université de Bordeaux I.

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This paper deals with the normal-coordinate analysis of the hexamolybdate anion. Vibrational spectra of $M_6O_{19}^{n-}$ anions (M = Nb^V, Ta^V, Mo^{VI}, W^{VI}) of the Lindqvist structure have been already reported.[2-6] Two studies[3,4] include a normal-coordinate analysis. However, the calculated force fields are based on approximate geometrical data and on assignments which are not in agreement in the two papers. Some experiments carried out in solution and in solid state have led to propose new more probable assignments in the low-frequency region.[6] In order to shed more light on the assignments of vibrations in these hexametalates and to calculate on this basis a more reasonable force field, it was justifiable to completely reconsider the normal-coordinate treatment, including isotopic substitution on metal and oxygen for determining more parameters in the force field. This paper gives the results obtained with the hexamolybdate $Mo_6O_{19}^{2-}$, which was particularly convenient for the possibility of preparation of isotopic derivatives (^{18}O, ^{92}Mo, and ^{100}Mo).

Experimental Section

(A) Preparations. All the preparations were based on the acidification of sodium molybdate according to the reaction

$$6MoO_4^{2-} + 10H^+ \rightarrow Mo_6O_{19}^{2-} + 5H_2O$$

Isotopic starting materials were purchased from the Commissariat à l'Energie atomique: ^{92}Mo (94.1%), ^{100}Mo (92.2%), $H_2{}^{18}O$ (99%), and $Mo^{18}O_3$ prepared by heating molybdenum powder in $^{18}O_2$ (99%) at about 700 °C.

For preparative procedures involving ^{18}O, experiments were carried out in a glovebox under argon ($O_2 < 5$ ppm, $H_2O < 5$ ppm). Dimethylformamide (DMF) (spectroscopic grade) was carefully dehydrated ($H_2O < 5 \times 10^{-4}$ M) by stirring on a type 4 Å molecular sieve and kept under argon. Diethyl ether (Et_2O) (analytical grade) was previously distilled over sodium and stirred on type 4 Å molecular sieve as above. Hydrochloric acid in DMF solution was obtained by bubbling hydrogen chloride (99.0%) into freshly dried DMF. All other reagents were analytical grade and used without further purification. Analyses were carried out for the natural compound by the Service central de Microanalyse du CNRS.

$[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$. The hexamolybdate of TBA (TBA = tetra-*n*-butylammonium) was prepared according to Fournier's method.[7] Anal. Calcd: C, 28.15; H, 5.28; N, 2.05; Mo, 42.2. Found: C, 27.69; H, 5.43; N, 2.05; Mo, 41.93.

$[(n\text{-}C_4H_9)_4N]_2Mo_6O_{19}$ with ^{92}Mo and ^{100}Mo. $Na_2MoO_4 \cdot 2H_2O$ with ^{92}Mo and ^{100}Mo was prepared from 100 mg of Mo metal according to Müller et al.[8] Preparation of $Mo_6O_{19}^{2-}$ as TBA salt was then conducted according to Fuchs.[9] Crude products were recrystallized from DMF.

$[(n\text{-}C_4H_9)_4N]_2Mo_6{}^{18}O_{19}$. A 1-g (50-mmol) sample of $H_2{}^{18}O$ and 10 mL of freshly dried Et_2O were introduced into a round-bottom flask surmounted by a long tube acting as a refrigerant. A 282-mg (12-mmol) sample of sodium,[10] cut into about 50 fragments, was progressively added to the mixture with stirring and allowed to be gently digested. Et_2O was used to avoid a violent reaction, to prevent water evaporation, and to diminish the viscosity of the reacting mixture. About half an hour was needed to prepare $Na^{18}OH$. A 923-mg (6.2-mmol) sample of powdered $Mo^{18}O_3$ was then added little by little with stirring. The progress of the reaction was followed thanks to the color of the solid which turned from greenish (MoO_3) to white (MoO_4^{2-}).

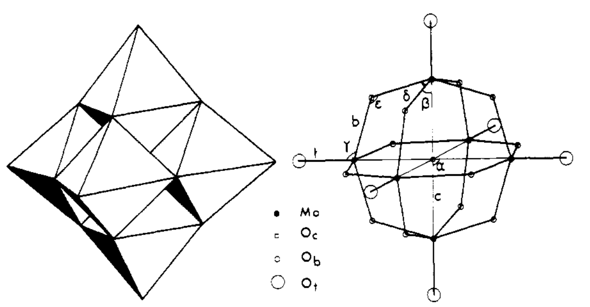

Figure 1. Idealized Mo_6O_{19} model of O_h symmetry (Lindqvist structure).

The suspension was then acidified by addition of 2.4 mL of 4.25 M HCl in DMF. The solution turned yellow, and the white precipitate (NaCl) was filtered off. Addition of 2.70 mL of 1 M TBABr in DMF to the filtrate induced the precipitation of yellow $TBA_2Mo_6{}^{18}O_{19}$ which was also filtered off. The resulting yellow filtrate was allowed to crystallize in the glovebox, but it turned green and deposited colorless crystals (β-octamolybdate) after a few weeks. Attempts to recrystallize crude $TBA_2Mo_6{}^{18}O_{19}$ in the glovebox failed as well. When the recrystallization was carried out in free air, well-defined yellow hexamolybdate crystals were obtained after a few days.[11] These crystals contained however at least two mixed isotopic species, as suggested by Raman spectroscopy.

The only suitable material for the vibrational study was then the crude yellow product.

(B) Spectral Measurements. IR spectra of solids were recorded on a Perkin-Elmer 283 spectrophotometer (1000–200 cm^{-1}) and a Grubb-Parsons Cube MK-II interferometer (350–50 cm^{-1}) as KBr, CsI, or polyethylene pellets. Solution spectra were made on a PE 283 spectrophotometer as capillary layers between CsI or CsBr plates.

Raman spectra were taken on a Coderg PH O spectrometer equipped with a Spectra Physics argon–krypton laser (514.5 nm, ~100 mW). Concentrated DMF solutions were sampled in 0.3-mL parallelepipedic glass cells or sealed capillary tubes. Solid spectra were obtained either directly from crystals or from powdered samples in sealed capillary tubes.

Samplings of the ^{18}O compound were achieved in the glovebox. Isotopic shifts were measured on spectra scanned under the same conditions on the same chart. The overlapping was easy to realize for the IR spectra owing to the flow-chart system of the PE 283 spectrophotometer, and this was controlled with plasma or DMF lines for the Raman spectra.

(C) Computations. The computations were achieved (double precision) on an IBM 370/168 computer by using programs based on Schachtschneider's method[12] and adapted by us for the treatment of a large molecule with a great number of internal coordinates.

Description of the Structure

The $Mo_6O_{19}^{2-}$ anion (O_h symmetry) is made up of a compact package of six edge-sharing octahedra. There are three nonequivalent types of oxygens, 6 terminal oxygens (O_t), 12 bridging oxygens (O_b), and 1 central oxygen (O_c), and three different types of Mo–O bonds, terminal Mo–O_t bonds, bridge Mo–O_b bonds, and central Mo–O_c bonds (Figure 1). Each Mo atom is displaced from the center of the corresponding MoO_6 octahedron, giving rise to long Mo–O_c bonds and short

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[10] An excess of water was required; attempts to perform the reaction with stoichiometric amount of water failed.

[11] These observations confirm that hexamolybdate needs some water for crystallizing from its solutions that contain octamolybdate in equilibrium with hexamolybdate. Anhydrous solutions slowly deposit the less soluble anion, i.e., the β-octamolybdate. Water, even in small amounts, favors the conversion octamolybdate → hexamolybdate, probably through intermediary less condensed molybdates, which explains the quick isotopic exchange in solution. Such an isotopic exchange does not occur on solid material.

[12] Schachtschneider, J. H. Technical Report 57-65; Shell Development Co.: Emeryville, CA.

Mo–O_t bonds. Such a tetragonal distorsion of MoO_6 octahedra preserves the O_h structure of the whole anion (molecular symmetry in the isolated zero-order approximation).

From the reported structural investigations,[13,14,15] it appears that the site symmetry of the anion in the crystal is considerably lower than O_h, namely, C_i. It is worth noticing that the actual geometry is however not far from O_h. However, the counterions used in these investigations are not suitable for the isotopic synthesis, especially for ^{18}O compound synthesis. We have therefore chosen the tetrabutylammonium counterion (TBA^+) which was convenient for this purpose. The structure of $TBA_2Mo_6O_{19}$, not yet solved, likely agrees with the above-mentioned ones, and the vibrational spectra of this salt are easily assigned in the O_h symmetry.

For these reasons, and keeping in mind that the normal-coordinate treatment is rather difficult even in the O_h symmetry, we decided to investigate the idealized Mo_6O_{19} model of O_h symmetry, with all the isotopic species being prepared as TBA salts. The molecular parameters have been adapted from Allcock's data[13] to fit with the O_h symmetry: Mo–O_c = 2.318 Å, Mo–O_b = 1.927 Å, and Mo–O_t = 1.677 Å.

Classification of Normal Modes. Internal Coordinates. The Mo_6O_{19} model of 25 atoms has 69 normal modes of vibration that are distributed between the symmetry classes of the O_h symmetry according to

$$\Gamma_{vib} = 3\ A_{1g}\ (R) + A_{2g}\ (\text{inact}) + 4\ E_g\ (R) + 3\ F_{1g}\ (\text{inact}) + 4\ F_{2g}\ (R) + A_{2u}\ (\text{inact}) + E_u\ (\text{inact}) + 7\ F_{1u}(IR) + 4\ F_{2u}\ (\text{inact})$$

Therefore 11 active modes are expected in the Raman spectra ($3\ A_{1g} + 4\ E_g + 4\ F_{2g}$) and 7 active modes in IR spectra ($7\ F_{1u}$).

The set of 162 internal coordinates (Figure 1) is defined

6 Mo–O_c bonds	c
6 Mo–O_t bonds	t
24 Mo–O_b bonds	b
12 MoO_cMo angles	α
24 O_cMoO_b angles	β
24 O_bMoO_t angles	γ
24 O_bMoO_b angles	δ
12 MoO_bMo angles	ϵ
6 torsional coordinates (dihedral angles between planes which have Mo–O_c as common line)	τ/c
24 torsional coordinates (dihedral angles between planes which have Mo–O_b as common line)	τ/b

Symmetry coordinates generated from the above internal coordinates can be constructed as long as redundancies are not involved. To clearly express the 93 redundant symmetry coordinates for such a highly condensed anion is really an inextricable problem. In the previous normal-coordinate treatments,[3,4] all the internal coordinates were not included in order to reduce the number of redundancies: so the MoO_cMo and MoO_bMo angles were not introduced, as well as the torsional angles. In this way, the redundancies related to the different rings were not considered. This procedure makes the problem less difficult, but it should be questioned since it does not take account of the bridge angles which are a characteristic feature of the anion.

Therefore, we preferred to introduce all the internal coordinates. Giving up the attractive but nonrealistic project of carrying out the mathematical treatment in symmetry coordinates, we have solved the problem in internal coordinates. In these conditions, the redundancies automatically vanished: 93 zero frequencies, i.e., as many as redundancies, were calculated.

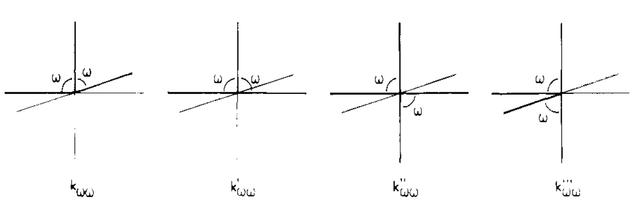

Figure 2. Conventions used for bend–bend interactions.

Normal-Coordinate Analysis. The GF method of Wilson et al.[16] was used to perform the normal-coordinate analysis. The G matrices (162,162) were constructed for the four isotopic species with the assumption of the same structural parameters and by varying only the atom masses. An internal valence force field was used to build the **F** matrix common to the four isotopic species. This matrix (162,162) involves the following force constants:

(i) Principal force constants: stretch force constants, k_c, k_b, k_t; bend force constants, k_α, k_β, k_γ, k_δ, k_ϵ; torsional force constants, $k_{\tau/c}$, $k_{\tau/b}$.

(ii) Stretch–stretch interactions between bonds having one common atom, with the exception of the t bonds: k_{cc} (cis interaction), k'_{cc} (trans interaction); k_{bb} (cis interaction), k'_{bb} (trans interaction), k''_{bb} (interaction between two adjacent octahedra); k_{ct}, k_{bt}, k_{cb}; k_{tt} (cis interaction), k'_{tt} (trans interaction).

(iii) Stretch–bend interactions (the interactions in which the bond is a side of the angle are only considered): $k_{c\alpha}$, $k_{c\beta}$, $k_{b\beta}$, $k_{b\gamma}$, $k_{b\delta}$, $k_{b\epsilon}$, $k_{t\gamma}$.

(iv) Bend–bend interactions (the interactions in which the angles have either a common side or a common central atom are only considered): $k_{\alpha\alpha}$, $k'_{\alpha\alpha}$, $k''_{\alpha\alpha}$, $k'''_{\alpha\alpha}$; $k_{\beta\beta}$, $k'_{\beta\beta}$; $k_{\gamma\gamma}$, $k'_{\gamma\gamma}$; $k'_{\delta\delta}$, $k''_{\delta\delta}$; $k_{\beta\delta}$, $k'''_{\beta\delta}$; $k'_{\beta\gamma}$, $k''_{\beta\gamma}$; $k'''_{\beta\gamma}$; $k_{\gamma\delta}$, $k'''_{\gamma\delta}$; $k_{\epsilon\beta}$, $k_{\epsilon\delta}$, $k_{\epsilon\gamma}$. Conventions are explained in Figure 2.

Vibrational Spectra and Assignments. The IR and Raman spectra of the $Mo_6O_{19}^{2-}$ anion (natural molybdenum and oxygen) are reported in Figure 3. The frequency shifts induced by ^{92}Mo–^{100}Mo and ^{16}O–^{18}O substitutions are listed in Table I.

Only six of the seven expected IR bands are apparently observed. However, the spectrum of hexamolybdate can be easily correlated with that of isostructural hexatungstate.[5,6] Therefore, the nonobserved seventh band has to be related to the weak 172-cm^{-1} band of $W_6O_{19}^{2-}$ and thus is expected below 200 cm^{-1}: it is likely too weak to be observed.

Raman spectra do not exhibit as well the expected number of bands. However, the three polarized A_{1g} bands are easily recognized. The medium-frequency one is weak and broad and could, from that fact, present some deformation character while the other two bands, intense and narrow, likely correspond to stretching modes.

To initiate the calculations, we have used a force field including some values published by Mattes et al.[4] and some additional values of principal force constants not introduced by these authors. This initial force field did not involve bend–stretch and bend–bend interactions. While these interactions were progressively introduced, after a few runs the force field reproduced all the observed frequencies of the natural compound, and the 432, 352, and 217-cm^{-1} IR bands were assigned, respectively, to the Mo–O_c stretch, the δ bend, and the γ bend. However, checking the force field with the isotopic derivatives made us realize that the assignments were

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Table I. Calculated and Observed Frequencies (cm^{-1}), Calculated and Observed $\Delta\nu_s$ Induced by ^{92}Mo–^{100}Mo and ^{16}O–^{18}O Substitution, and Potential Energy Distribution (PED)

sym and activity			frequencies					$\Delta\nu(^{92}$Mo–^{100}Mo)		$\Delta\nu(^{16}$O–^{18}O)		
			calcd				obsd					
R	IR	inact	Mo ^{16}O	^{92}Mo ^{16}O	^{100}Mo ^{16}O	Mo ^{18}O	Mo ^{16}O	calcd	obsd	calcd	obsd	PED (values higher than 5%)
A_{1g}			986	989	983	939	986	6.4	6.5 ± 0.5	47.2	46 ± 0.5	$93 t$
E_g			958	960	957	908	958	3.1	4.5 ± 1	50.3	48 ± 1	$87 t$
	F_{1u}		956	958	954	908	956	4.2	4 ± 0.5	48.5	48 ± 0.5	$93 t$
E_g			817	819	815	777	817	4.8	*a*	40.1	45 ± 10^b	$48 b + 18 t + 11 \gamma$
	F_{1u}		795	797	793	754	796	3.5	4 ± 1	40.6	40 ± 1	$53 b + 13 \gamma + 11 t$
		F_{2u}	764	765	764	721		0.3		43.3		$58 b + 16 \gamma$
		A_{2g}	764	764	764	720		0.0		43.7		$62 b + 8 \gamma$
		F_{1g}	750	751	750	709		0.8		41.6		$63 b + 18 \gamma$
F_{2g}			601	602	599	570	?	2.7		30.7		$101 \gamma + 26 b + 6 \epsilon$
	F_{1u}		599	601	597	570	598	3.8	4 ± 1	29.0	28 ± 1	$78 \gamma + 30 b$
A_{1g}			598	600	596	569	598	3.9	*a*	28.8	20 ± 10^b	$42 \gamma + 23 b + 20 \epsilon$
		F_{2u}	547	550	545	524		5.3		23.9		$89 \gamma + 44 b + 5 \epsilon$
		F_{1g}	505	510	501	488		8.5		17.2		$77 \gamma + 32 b$
E_g			439	440	438	416	?	1.5		23.3		$61 \gamma + 59 b + 30 \epsilon$
	F_{1u}		432	435	429	415	432	5.7	7 ± 1	16.4	16 ± 0.5	$40 \gamma + 13 b + 11 \epsilon + 8 \delta$
		A_{2u}	387	387	387	365		0.0		22.1		69δ
	F_{1u}		351	352	350	334	352	2.6	2 ± 0.5	16.7	17 ± 0.5	$70 c + 8 b$
F_{2g}			337	337	336	318	?	0.6		18.3		$60 \delta + 6 b + 6 \epsilon$
		F_{2u}	299	299	298	283		1.0		15.8		$81 b + 54 \gamma + 46 \epsilon$
A_{1g}			285	289	281	279	285	8.2	8.5 ± 0.5	5.4	3.5 ± 1	$80 b + 7 c$
	F_{1u}		216	218	214	209	217	4.0	2 ± 1	7.2	8 ± 1	$170 b + 7 \epsilon + 6 c$
E_g			213	216	210	209	?	6.2		4.0		$79 b + 30 \gamma + 13 c$
F_{2g}			206	206	205	196	205	1.5	2.5 ± 0.5	9.6	10 ± 1	$58 b + 55 \epsilon + 29 \delta$
		E_u	193	193	193	182		0.0		11.0		66δ
	F_{1u}		168	168	168	159	?	0.3		9.1		$150 \delta + 32 c + 14 b + 9 \gamma$
F_{2g}			161	163	158	158	166	5.0	*a*	3.3	*a*	$337 b + 20 \delta + 15 \epsilon$
		F_{1g}	151	151	151	144		0.3		7.1		112δ
		F_{2u}	139	141	137	136		4.0		2.8		$167 b + 26 \delta$

[a] Difficult to establish (weak lines, low concentration). [b] Large inaccuracy related to the weakness and broadness of the lines.

wrong in the low-frequency region.

The strong IR band at 432 cm^{-1}, assigned by Mattes et al.[4] to asymmetric Mo–O$_c$ stretch, is indeed very sensitive to molybdenum substitution ($\Delta\nu(^{92}$Mo–^{100}Mo) ≈ 7 cm^{-1}), and the calculated frequency corresponding to this motion was only slightly affected by this substitution (~1–2 cm^{-1}). R.T.[6] had already shown that this band is strongly shifted from solid to solution, which is not consistent with a motion involving internal atoms. It was then impossible to assign the 432-cm^{-1} band to the c stretch.

The calculations showed that four low-frequency F_{1u} bands had respectively predominant characters of γ bend, c stretch, b stretch, and δ bend and that the low-frequency A_{1g} line presented some c-stretch character. All the assignment permutations were tried out with a careful check of the fit between observed and calculated isotopic shifts induced by molybdenum and oxygen substitition. It was remarkable that, even with force fields based on wrong assignments in the low-frequency region, the k_t value did not vary significantly, and the three highest frequency modes, related to almost pure Mo–O$_t$ stretchings, were always well placed, with correct isotopic shifts.

After a rather tedious treatment, the only possible assignments for the 432- and 352-cm^{-1} bands were, respectively, the γ bend and c stretch. When the 217-cm^{-1} band was assigned to the δ bend, the nonobserved IR band was calculated at about 240 cm^{-1}, in contrast to the value expected below 200 cm^{-1}. A new permutation was then made, with assignment of the nonobserved band to the δ bend. On this basis, the field was adjusted by assigning the 205-cm^{-1} Raman band to a F_{2g}-type motion, rather than an E_g-type one, according to the isotopic shifts. Taking into account that the observables are subject to experimental errors, we stopped the refinement when a reasonable fit between the calculated and observed $\Delta\nu_s$ was reached. As we propose almost as many force field parameters as observables, when we know that the observables are not independent, our force field is slightly overestimated. Therefore a further refinement by using a least-squares method would not bring more significant informations and was thus not carried out.

Table II. Internal Valence Force Field[a]

k_c	0.47 (0.83)	k_α	0.00	$k'_{\delta\delta}$	−0.05
k_b	2.35 (3.50)	k_β	0.03	$k''_{\delta\delta}$	0.10
k_t	7.46 (7.30)	k_γ	2.73 (0.50)	$k_{\beta\delta}$	0.10
k_{cc}	0.03	k_δ	0.49 (0.19)	$k'''_{\beta\delta}$	−0.05
k'_{cc}	−0.03	k_ϵ	0.69	$k'_{\beta\gamma}$	−0.15
k_{bb}	0.10 (0.40)	$k_{\tau/b}$	0.00	$k''_{\beta\gamma}$	−0.04
k'_{bb}	0.48 (0.60)	$k_{b\beta}$	−0.08	$k'''_{\beta\gamma}$	−0.16
k''_{bb}	−0.65 (0.20)	$k_{b\gamma}$	0.45 (0.10)	$k_{\gamma\delta}$	−0.05
k_{ct}	0.10	$k_{b\delta}$	0.15	$k'''_{\gamma\delta}$	−0.15
k_{bt}	0.53 (0.50)	$k_{b\epsilon}$	0.43	$k_{\epsilon\beta}$	−0.17
k_{cb}	0.07	$k_{t\gamma}$	0.36	$k_{\epsilon\delta}$	−0.06
k_{tt}	0.10 (0.10)	$k_{\gamma\gamma}$	0.30	$k_{\epsilon\gamma}$	−0.01
k'_{tt}	0.08	$k'_{\gamma\gamma}$	−0.15		

[a] All force constants are in mdyn Å^{-1} (=10^{-2} N m^{-1}). See text for explanation of the symbolism. Values in parentheses are drawn from Mattes et al.[4]

The observed and calculated frequencies and the assignments in terms of potential energy distribution (PED) are summarized in Table I. The "final" force field is listed in Table II. The description of the three A_{1g} modes according to the eigenvectors is presented in Figure 4.

Discussion

Owing to the considerations developed above, the proposed force field is only a reasonable approximate one. It is, however, better than Mattes' one, which failed to predict correct isotopic shifts. It is worth noticing that isotopic substitutions allowed us to correct erroneous assignments and to get a force field that accounts for all the experimental data.

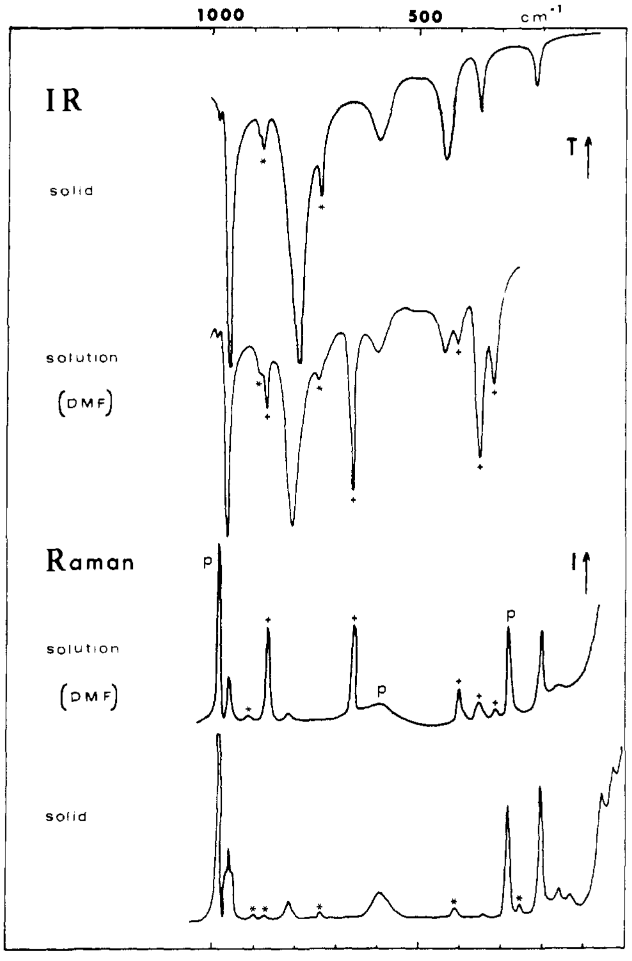

Figure 3. IR and Raman spectra of $Mo_6O_{19}^{2-}$: (*) vibration modes of TBA^+; (+) vibration modes of solvent (DMF); (p) polarized line.

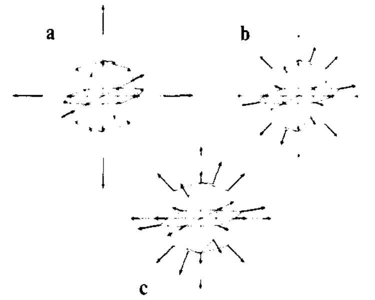

Figure 4. Description of the three A_{1g} modes (arrows show quantitatively the atom displacements in arbitrary units): (a) 986 cm^{-1}; (b) 598 cm^{-1}; (c) 285 cm^{-1}.

Therefore the discussion will be restricted to principal force constants and stretch–stretch interactions. All the other interactions have inaccurate values on which any discussion is meaningless. The numerical values listed in Table II correspond to those required for the closest fit.

(i) Stretching Force Constants. The k_t value does not strongly differ from that of Mattes et al.[4] (see Table II). It agrees with a rather short bond with some multiplicity character. Let us point out that this value fits well with the correlation curve (k_{Mo-O} vs. Mo–O bond length) established by Cotton et al.[17]

As mentioned above, the three bands above 950 cm^{-1} are almost pure $Mo-O_t$ stretchings. The concept of high-frequency separation holds well for these modes, which can be correctly described as $\nu_s(Mo-O_t)$ (A_{1g}) and $\nu_{as}(Mo-O_t)$ (E_g and F_{1u}).

Interaction force constants k_{tt} and k'_{tt} were required to account for the $\nu_s-\nu_{as}$ splitting, as previously noticed by Farrell et al.[3] and Mattes et al.:[4] without them, the three $\nu(Mo-O_t)$ modes were always calculated at about the same frequency. Although not so high as k_{tt} in mononuclear oxo complexes such as $MoO_2F_4^{2-}$ and $MoO_3F_3^{3-}$,[18] their values express a slight electronic transmission through the $O_t-Mo-O-Mo-O_t$ chains.

The other two stretching force constants k_b and k_c strongly differ from those obtained by Mattes and those derived from the Cotton's correlation curve. The higher values found by Mattes are directly related to the incorrect assignments in the medium- and low-frequency regions.

The k_b value agrees with that calculated for a single covalent bond according to Siebert's formula.[19] Thus the $Mo-O_b$ bonds can be considered as single bonds, which could be also derived from the correlation curve (bond length vs. bond order) proposed by Schröder.[20]

The very low k_c value allows very loose $Mo-O_c$ bonds to be assumed, which is consistent with the rather long $Mo-O_c$ distance. It is difficult to describe the nature of the $Mo-O_c$ bonds because of the unusually hexacoordinated O_c atom. The $Mo-O_c$ bonds could be assumed to be pure ionic bonds or, in an alternative description, delocalized multicenter bondings involving the six molybdenum atoms. In both descriptions, the O_c atom is effectively loosely bonded.

Many bands account for $Mo-O_b$ stretchings, as seen in the PED column of Table I. None can be described as pure $Mo-O_b$ stretch since even the E_g 817-cm^{-1} and F_{1u} 796-cm^{-1} modes, previously described as pure $Mo-O_b$ stretchings, present some t-stretch and γ-bend characters. It clearly appears, from geometrical considerations and from calculations, that all the vibrations involving $Mo-O_b$ stretchings are not pure. Notice, in particular, the A_{1g} 285-cm^{-1} mode, previously described as a $Mo-O_c$ stretch, which is better assigned as a motion involving both $Mo-O_b$ and $Mo-O_c$ stretches (Figure 4c) without any character of deformation, as suggested by the narrow and intense corresponding Raman line. This mode can be considered as a pulsation or "breathing" of the polyanionic framework around the O_c atom, which effectively reduces to the ν_1 (A_{1g}) vibration of the O_cMo_6 octahedron, when only this central octahedron is considered.

It appears that the ν_{as} $Mo-O_c$ mode, which had to be assigned to the F_{1u} 352-cm^{-1} band, is a rather pure one, as already proposed by Thouvenot.[6] This mode can be easily correlated to a vibration of the O_cMo_6 octahedron: it can be tentatively described as a vibration of the central oxygen atom within the framework.

The interaction constant k''_{bb} relative to $Mo-O_b$ oscillators with a common O_b atom (MoO_bMo bridges) is found to be negative. On the other hand, the interaction constants relative to Mo–O oscillators with a common Mo atom are all positive, which is consistent with results observed by Cotton and Wing[17] on simple species. The trans k'_{bb} value is higher than the cis k_{bb} value, as usually observed. The cis stretch–stretch interaction constants decrease in the $k_{bt}-k_{bb}-k_{cb}$ sequence, which is paralleled by the $k_t-k_b-k_c$ decreasing one. An attempt to correlate the interaction constants k_{rR} to the principal stretch constants k_r and k_R was made by using the empirical relation $k_{rR} = a(k_rk_R)^{1/2}$ proposed by Mattes.[21] However, it failed since the proportionality factor a varies within too wide a limit (0.04–0.28).

(ii) Bending Force Constants. The most significant feature is perhaps the surprisingly high value of k_γ corresponding to the O_tMoO_b bending: the k_γ value even exceeds the k_b value

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[20] Schröder, F. A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2294.

[21] Mattes, R. *Z. Anorg. Allg. Chem.* **1971**, *382*, 163.

corresponding to the b stretch. This has to be related with the high stretching force constant k_t and the high electronic density carried by the Mo–O_t bonds. When considering that the bending constant reflects the ability of electronic densities carried by adjacent bonds to repell each other, it is easy to understand that higher localized electronic density (i.e., more dense valence orbitals in the VSEPR approach) will induce a higher bending constant.

On the other hand, the bending constant k_β has a very low value consistent with the very loose Mo–O_c bonds, carrying a very low electronic density. The k_δ value cannot be given accurately because of the nonobservation of the F_{1u} band assigned to δ bending. Since this band is expected below 200 cm^{-1}, k_δ is certainly less than 0.5 mdyn $Å^{-1}$, which is also consistent with a bend constant of an angle between two single bonds, Mo–O_b.

So far as the k_α value is concerned, we observe that the replacement of 0.005 by 0.00 does not affect significantly the calculated frequencies. We only can say that k_α has a very low value, which is again consistent with the loosely bonded O_c atom.

The four above bend constants concern each MoO_6 octahedron and the O_cMo_6 octahedron of the framework. The k_ϵ constant gives information about the ability of deformation of the MoO_bMo angles between two adjacent octahedra, i.e., the bridge angles characteristic of the structure. Its value is as well consistent with the single-bond character of the Mo–O_b bonds. Let us notice that k_ϵ is higher than k_δ. This could be related to the electronic density along the Mo–O_b bonds: the electronic cloud should be more dense around the O_b atoms.

When considering the PED column of Table I, we can see that, except for δ bending, there are no pure bending modes. The γ bend significantly contributes to many modes at relatively high frequency. It even appears that the F_{1u} 598-cm^{-1} and A_{1g} 598-cm^{-1} modes, previously assigned as Mo–O_b stretching modes, present a predominant γ character, with some b-stretch character. The other bend modes appear as mixed modes in the medium- and low-frequency regions. The ϵ character is never predominant, as seen in Table I.

(iii) Torsional Constants. The torsions over c bonds were always found to be unnecessary. The torsions over b bonds act in some low-frequency vibrations. However, the values 0.02 and 0.00 mdyn $Å^{-1}$ practically lead to the same results. We must admit there is no serious basis for discussion of such a low-value force constant: it is better to neglect it.

Conclusion

In this paper devoted to the normal-coordinate analysis of hexamolybdate anion of the Lindqvist structure, we have demonstrated the importance of using isotopic molecules as a support of assignments. The outstanding feature of this study is certainly the complete assignment of the vibrational spectra of this anion.

On this basis, we were able to propose a reasonable force field which accounts for all the experimental data (four isotopic species). The three stretching force constants k_t (7.46 mdyn $Å^{-1}$), k_b (2.35 mdyn $Å^{-1}$), and k_c (0.47 mdyn $Å^{-1}$) are consistent with double Mo–O_t bonds, single Mo–O_b bonds, and very loose Mo–O_c bonds, respectively.

From this study, by assumption of the transferability of the force field, investigations on other polyoxometalates will be carried out.

Acknowledgment. We wish to thank the late Dr. M. T. Forel, who encouraged us to undertake this study, and Dr. M. Fournier for helpful discussions about polyoxometalates: success in synthetizing the ^{18}O derivative was certainly due to his valuable advice.

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Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208

Microwave, Infrared, and Raman Spectra, Structure, Quadrupole Moment, and Normal-Coordinate Analysis of Disilyl Iodide[1]

J. R. DURIG,* J. S. CHURCH, and Y. S. LI

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The microwave spectra of H_3SiSiH_2I and D_3SiSiD_2I have been recorded from 26.5 to 38.5 GHz. *a*-Type transitions were observed, and R-branch assignments have been made for the ground vibrational state. The rotational constants were found to have the following values: for H_3SiSiH_2I, $A = 8602.22 \pm 8.63$, $B = 1179.79 \pm 0.02$, $C = 1062.47 \pm 0.02$ MHz; for D_3SiSiD_2I, $A = 6571.01 \pm 5.80$, $B = 1078.87 \pm 0.03$, $C = 969.96 \pm 0.06$ MHz. From a diagnostic least-squares adjustment to fit the six rotational constants, the following structural parameters were obtained: $r(\text{Si–H}_3) = 1.491 \pm 0.010$ Å, $r(\text{Si–H}_2) = 1.478 \pm 0.010$ Å, $r(\text{Si–Si}) = 2.336 \pm 0.007$ Å, $r(\text{Si–I}) = 2.440 \pm 0.009$ Å, $\angle\text{SiSiI} = 106.7 \pm 0.3°$, $\angle\text{SiSiH(I)} = 111.8 \pm 1.8°$, $\angle\text{SiSiH} = 111.3 \pm 1.9°$. These parameters are compared to the corresponding ones in some other silanes. The quadrupole coupling constants were found to have the values $\chi_{aa} = -938$, $\chi_{bb} = 255$, and $\chi_{cc} = 683$ MHz with $\eta = -428$ MHz. The infrared (3500–20 cm^{-1}) and Raman spectra (3500–0 cm^{-1}) have been recorded for both the gas and solid. Additionally, the Raman spectra of the liquids were recorded and qualitative depolarization values were obtained. All of the normal modes except the SiH_3 torsion have been assigned on the basis of band contours, depolarization values, and group frequencies. A normal-coordinate calculation has been carried out by utilizing a modified valence force field to calculate the frequencies and the potential energy distribution. Some mixing was found among the SiH_3 symmetric deformation, the SiH_2 scissors, and the SiH_2 wagging motions. These results are compared to similar quantities in some corresponding molecules.

Introduction

Disilyl iodide was first prepared and isolated by Ward and MacDiarmid[2a] in 1959. Prior to this time, the only other monohalogenated disilyl compounds reported were H_3SiSiH_2Br and H_3SiSiH_2Cl.[2b,3] Neither of these compounds was obtained in high purity, and because of the proposed ready

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[1] Taken in part from the thesis of J. S. Church, which will be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

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[3] J. M. Gamboa, *An. Real Soc. Esp. Fis. Quim., Ser. B*, **46**, 699 (1950); *Chem. Abstr.* **49**, 6766 (1955).

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