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Estimation of the Dissolved Structures and Condensation Reactivities of Mononuclear Molybdenum(VI) Species in Solution Using the UV-vis Absorption Spectra and Molecular Orbital Calculation DV-$X\alpha$

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The dissolved structures of the mononuclear molybdate species, $MoO_4{}^{2-}$, $HMoO_4{}^-$, and H_2MoO_4, in aqueous solution were estimated by optimizing their structure models so that their UV-vis absorption spectra were well reproduced by the DV-$X\alpha$ molecular orbital calculation. In this paper it is proposed that the former two species are tetrahedral ions, and the last is a distorted octahedral species. Using the values of the bond order obtained by a Mulliken population analysis the reason why the dimolybdate anion $Mo_2O_7{}^{2-}$ does not exist, in contrast with the presence of the well-known dichromate anion $Cr_2O_7{}^{2-}$, has been explained. The key species which plays an important role in condensation reactions of molybdate system is not the $HMoO_4{}^-$ ion, but the H_2MoO_4 with very weak Mo–OH bonds.

The molybdate(VI) ion, $MoO_4{}^{2-}$, is easily protonated and aggregated to form a variety of monomers and polymers in an acidified solution. Many studies on the dissolved species have been reported.[1—12] Recently, potentiometric data for acidified solutions have been reevaluated; several equilibria models have been proposed with values of the equilibrium constants, which include the following anionic and neutral species: $MoO_4{}^{2-}$, $HMoO_4{}^-$, H_2MoO_4, $HMo_2O_7{}^-$, $Mo_7O_{24}{}^{6-}$, $HMo_7O_{24}{}^{5-}$, $H_2Mo_7O_{24}{}^{4-}$, $Mo_8O_{26}{}^{4-}$, etc.[6,7,9] In alkaline solutions, the molybdate ion exists as a tetrahedral inert ion, $MoO_4{}^{2-}$. When a dilute solution is acidified, protonation yields a hydrogenmolybdate ion, $HMoO_4{}^-$, and a dihydrogen molybdate (molybdic acid), H_2MoO_4.

Schwarzenbach and Meier[1] have proposed that a tetrahedrally symmetrical ion, $MoO_4{}^{2-}$, is transformed into an octahedrally symmetrical species, $Mo(OH)_6$, through $HMoO_4{}^-$; the increase in coordination number takes place during the acidification of $MoO_4{}^{2-}$ to $HMoO_4{}^-$:

$$MoO_4{}^{2-}\ (T_d) \rightarrow MoO(OH)_5{}^-\ (O_h) \rightarrow Mo(OH)_6\ (O_h) \qquad (1)$$

According to them, the intermediate octahedral species, $MoO(OH)_5{}^-$ ($=HMoO_4{}^-+2H_2O$), is unstable; and instability of this species is the cause of various condensation reactions.

Afterward, a considerable negative volume change for the second protonation ($HMoO_4{}^- \rightarrow H_2MoO_4$) has been reported by Cruywagen et al.,[5] and is ascribed to a decrease in the bulk free water and an increase in the coordination of a central atom by hydration. Furthermore, from the negative value of the entropy change of the second protonation (ca. -88 $J\,mol^{-1}\,K^{-1}$) and the positive value of the first protonation ($MoO_4{}^{2-} \rightarrow HMoO_4{}^-$: ca. 142 $J\,mol^{-1}\,K^{-1}$), the following change of the coordination sphere has been proposed:[5]

$$MoO_4{}^{2-}\ (T_d) \rightarrow HMoO_4{}^-\ (T_d) \rightarrow Mo(OH)_6\ (O_h) \qquad (2)$$

On the other hand, although the presence of dichromate ion, $Cr_2O_7{}^{2-}$, is well-known in a highly concentrated solution ($>10^{-4}$ $mol\,dm^{-3}$) of pH 1—5,[13] the presence of the anionic dimer of the molybdate has not been known for many years. Cruywagen has proposed that the addition of a dimeric anion with a mono-negative charge, $HMo_2O_7{}^-$, to an equilibria model markedly improves the fitting of the potentiometric data;[6,10] Tytko et al. have also proposed that small aggregated anions, such as dimer, trimer, and tetramer, seem to exist at very low concentrations of both molybdenum(VI) and an ionic medium.[9]

In order to understand why the reactivity of the molybdate ion and that of the chromate ion upon condensation reactions are different, details concerning the electronic states of dissolved mononuclear species in solution must be examined. To determine the electronic state, it is required to know the exact dissolved structure of the species. Methods such as X-ray diffraction, neutron diffraction, and EXAFS are not adequate for a solution system containing a very low concentration of target species. The fact that the amount of the $HMoO_4{}^-$ ion is only 20 to 30% of the total molybdate ion, even under the optimum condition, makes characterizing the species difficult.[12]

The ultraviolet/visible (UV/vis) absorption spectra, however, come from electronic transitions between molecular-orbital levels of the species. Any change in the structure of an ion induces a change in its UV-vis spectrum. In our previous reports[13,14] it has been demonstrated that a structure model of the species can be properly estimated so that the spectrum reproduced from an MO calculation using the model comes to fit its observed spectrum.

In this study, several possible structures of molybdenum(VI) ions were assumed, as shown in Fig. 1; and the most probable structure for each species was estimated.

Experimental

The UV-vis absorption spectra of solutions of 3×10^{-5} mol dm^{-3} Na_2MoO_4 with various pH values (from 1.97 to 5.38) adjusted with $HClO_4$ were measured. All of the reagents used were of analytical-grade chemicals. In this study, the ionic strength was not adjusted in order to avoid interactions between the molybdate ion and other chemicals.

Due to the complexity of the chemical equilibria, only the spectrum of $MoO_4{}^{2-}$ can be determined directly. The pure-component spectra of $HMoO_4{}^{-}$ and H_2MoO_4 were extracted by applying a chemometrical technique, a factor analysis with equilibrium constraints (FAEC),[12] to the spectra. The obtained component spectra are shown in the upper panels of Figs. 2, 4, and 5; they are in good agreement with those reported by Rohwer and Cruywagen.[4,10]

In order to obtain correct peak positions from the spectrum, a peak-separation treatment was carried out for each component spectrum after the abscissa was altered from the nm-unit into the eV-unit. Here, a peak was modeled with a product function of a Gaussian and a Lorentzian,

$$I(E) = H\exp\left(-B_G(E-E_0)^2\right) / \left[1+B_L(E-E_0)^2\right], \qquad (3)$$

where B_G and B_L are the half-width parameters of the Gaussian part and the Lorentzian part, respectively. The H is the peak height at the peak center position (E_0).[13]

Computational Method

The MO calculation was carried out using the discrete-variational $X\alpha$ (DV-$X\alpha$) method; the details concerning this method have been described elsewhere.[15] In the Hartree–Fock–Slater model, the exchange-correlation term is given by

$$V_{xc}(r) = -3\alpha[(3/8\pi)\rho(r)]^{1/3}, \qquad (4)$$

where $\rho(r)$ is the local charge density and α is the exchange scaling parameter; the value α=0.70 was used for all atoms throughout the present calculations.[16] In this method, an approximate self-consistent molecular potential is determined from the Mulliken gross orbital populations.

The excitation energy from the ith orbital to the jth orbital is given as the difference in the corresponding eigenvalues, $e_j - e_i$, for a 'transition-state' calculation, where a half electron is removed from the ith orbital and is put into the jth orbital. The evaluation of the peak intensity was carried out using the probability for spontaneous photon emission in the dipole transition.

Once the peak energy and the intensity are estimated, a theoretical line spectrum is obtained.[13,14] In order to make the comparison easy between the obtained component spectrum and the reproduced line spectrum, the latter is convoluted by Eq. 3 with appropriate half width parameters. The parameters

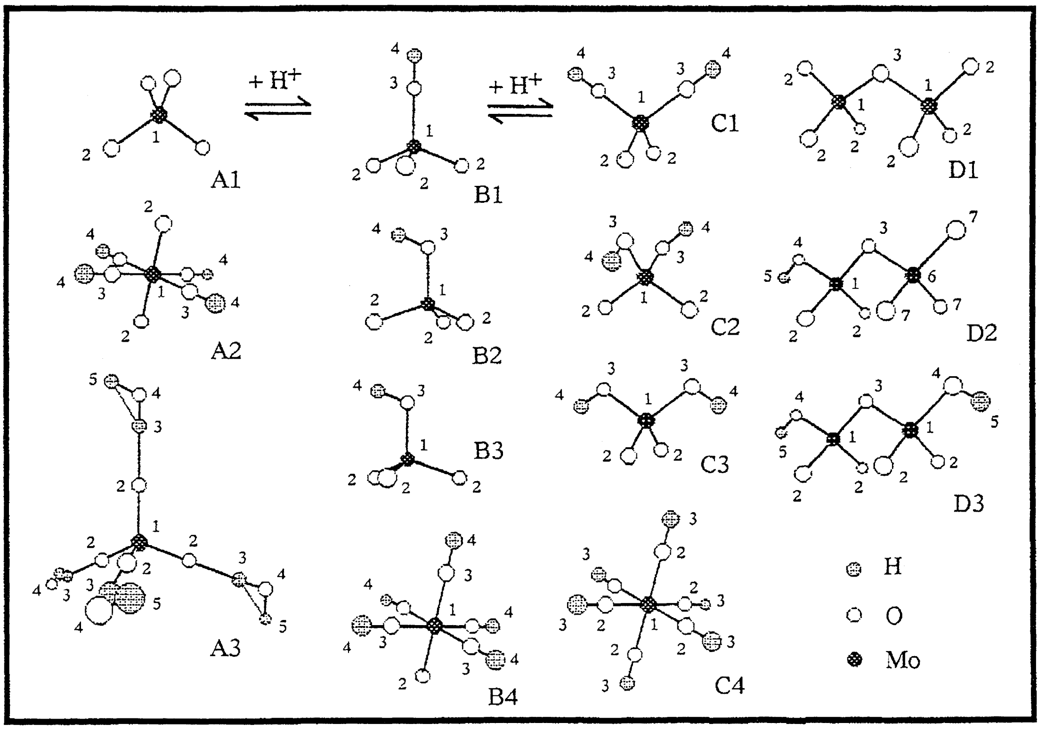

Fig. 1. Illustrations of cluster models used for the molecular orbital calculations: The values of bond lengths are listed in Table 1. And bond angles used here are either 180° or 109°28′.

$B_G=16.0$, $B_L=0$ were used throughout this study.

The Mulliken population analysis gives the bond-overlap population, called the bond order, which is a measure of the strength of covalency. Although the DV-$X\alpha$ method is not suitable for the calculation of accurate total energy, the bond order gives a good criterion concerning the stability of a cluster.[13)]

The numerical basis functions are used for the DV-$X\alpha$ calculation; the present basis set includes Mo 1s-5p, O 1s-2p and H 1s. A (Sony NWS 3860) work-station was used for the DV-$X\alpha$ calculation, and an NEC9801 for data treatment.

Results and Discussion

Cluster Model of MoO_4^{2-} Giving the Best Fit to the UV-vis Spectrum. In Fig. 2, the obtained component spectrum of the molybdate ion, MoO_4^{2-}, and the result of peak separation are shown along with the spectra reproduced by an MO calculation assuming the A1, A2, and A3 clusters of Fig. 1. The values of the bond lengths for clusters A1 and A2 are listed in Table 1. The structure of MoO_4^{2-} has been reported as the tetrahedral (T_d) with a molybdenum atom at the center and four oxygen atoms at the corners from a structure analysis of crystalline salts.[17,18)] It corresponds to cluster A1 of Fig. 1. The octahedral (O_h) structure shown in A2 of Fig. 1 was also examined for a comparison. Cluster A2 is $MoO_2(OH)_4^{2-}$, which has the same elemental composition as $MoO_4^{2-}(H_2O)_2$. Furthermore, a hydrated T_d species, shown as A3, was also examined.

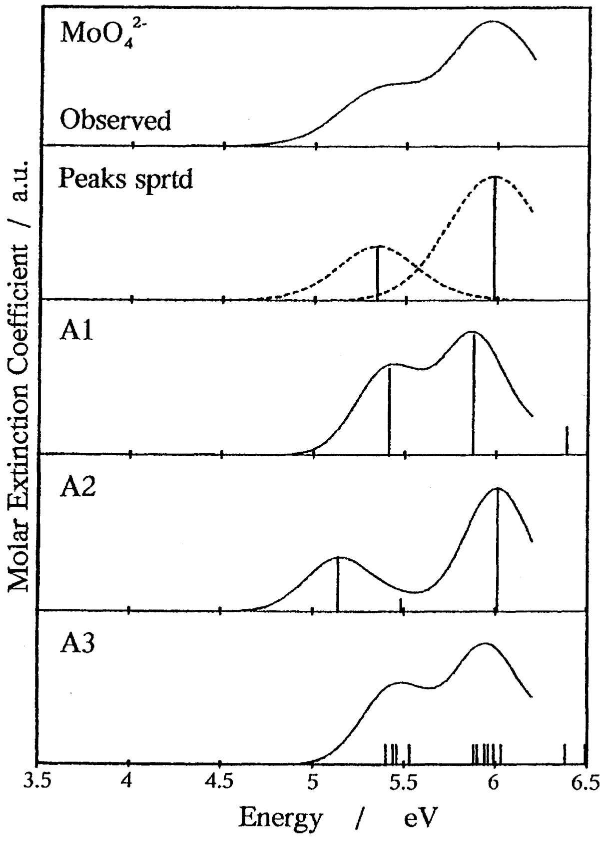

Fig. 2. First panel: component spectrum of molybdate ion MoO_4^{2-}; the second panel: result of peak separation; and the spectra reproduced from DV-$X\alpha$-MO calculation using the cluster models, A1, A2, and A3.

The conventional structure analysis applied to crystals containing MoO_4 units has shown that the distance between the Mo atom and the O atom is about 1.80 Å.[17,18)] If this distance was used for cluster A1, the molecular orbital levels were obtained as shown in Fig. 3. The molecular level $1t_1$ is the highest occupied orbital, and 3e is the lowest unoccupied orbital. Occupied orbitals mainly consist of the 2p orbital of oxygen atoms; and unoccupied orbitals mainly comprise 4d orbitals of the Mo atom. Thus, the electronic transitions are due to charge-transfer transitions from the oxygen 2p to the molybdenum 4d.

The transition energy strongly depends upon the distance between the Mo atom and the O atom: As the distance is made shorter, the transition energy from the HOMO to the LUMO becomes larger and the corresponding photon energy (peak) position shifts to the higher direction in major cases.[14)] Thus, the distance can be adjusted so that the calculated spectral peak (or a group of peaks) of the lowest energy coincides with the observed one. The Mo–O distance 1.80 Å is found to be the preferable value in this case. This distance is close to the Mo–O bond length reported from the crystal structure analysis.[17,18)]

The bond order obtained from a Mulliken population analysis is a measure of the covalent bond character. The large positive value means a strong covalent bond. The negative

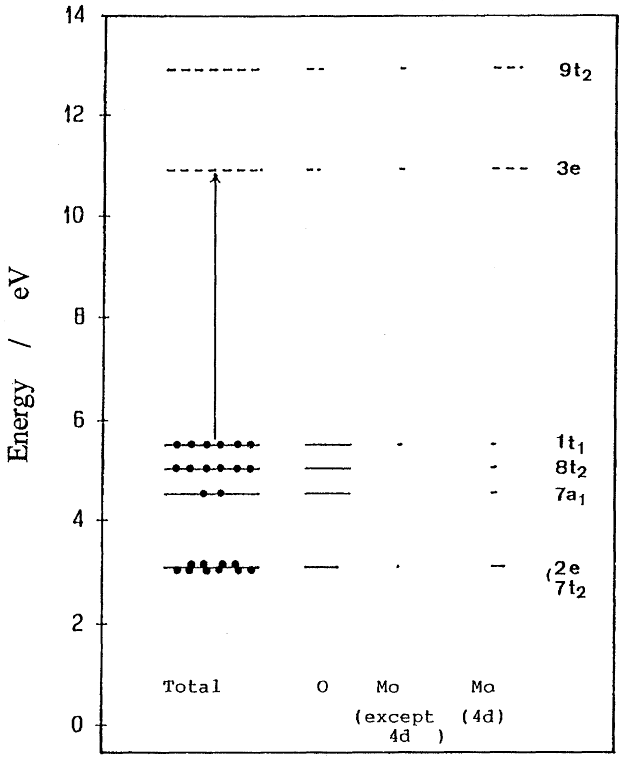

Fig. 3. Energy levels of the MoO_4^{2-} species with Mo–O distance 1.80 Å at transition state cluster A1; and the contributions of atomic orbitals.

Table 1. The Values of Bond Length, Net Charge, and Bond Order

Structure		Inter atomic distance/Å		Net charge				Bond order	
MoO_4^{2-}									
	A1	Mo(1)–O(2)	1.80	Mo(1)	+2.404	O(2)	−1.101	Mo(1)–O(2)	0.259
	A2	Mo(1)–O(2)	1.62	Mo(1)	+4.170	O(2)	−1.367	Mo(1)–O(2)	−0.456
		Mo(1)–O(3)	1.64	H(4)	+0.491	O(3)	−1.350	Mo(1)–O(3)	−0.874
		O(3)–H(4)	0.96					O(3)–H(4)	0.518
$HMoO_4^-$									
	B1	Mo(1)–O(2)	1.78	Mo(1)	+2.400	O(2)	−0.899	Mo(1)–O(2)	0.348
		Mo(1)–O(3)	1.96	H(4)	+0.509	O(3)	−1.211	Mo(1)–O(3)	0.062
		O(3)–H(4)	0.96					O(3)–H(4)	0.542
	B2	Mo(1)–O(2)	1.77	Mo(1)	+2.317	O(2)	−0.889	Mo(1)–O(2)	0.322
		Mo(1)–O(3)	2.09	H(4)	+0.437	O(3)	−1.086	Mo(1)–O(3)	0.189
		O(3)–H(4)	0.96					O(3)–H(4)	0.522
	B3	Mo(1)–O(2)	1.77	Mo(1)	+2.316	O(2)	−0.888	Mo(1)–O(2)	0.321
		Mo(1)–O(3)	2.09	H(4)	+0.430	O(3)	−1.081	Mo(1)–O(3)	0.189
		O(3)–H(4)	0.96					O(3)–H(4)	0.533
	B4	Mo(1)–O(2)	1.76	Mo(1)	+3.498	O(2)	−0.945	Mo(1)–O(2)	0.237
		Mo(1)–O(3)	1.81	H(4)	+0.513	O(3)	−1.224	Mo(1)–O(3)	−0.174
		O(3)–H(4)	0.96					O(3)–H(4)	0.530
H_2MoO_4									
	C1	Mo(1)–O(2)	1.78	Mo(1)	+2.569	O(2)	−0.716	Mo(1)–O(2)	0.397
		Mo(1)–O(3)	1.85	H(4)	+0.580	O(3)	−1.149	Mo(1)–O(3)	0.033
		O(3)–H(4)	0.96					O(3)–H(4)	0.511
	C2	Mo(1)–O(2)	1.74	Mo(1)	+2.426	O(2)	−0.723	Mo(1)–O(2)	0.410
		Mo(1)–O(3)	1.78	H(4)	+0.533	O(3)	−1.024	Mo(1)–O(3)	−0.020
		O(3)–H(4)	0.96					O(3)–H(4)	0.496
	C3	Mo(1)–O(2)	1.74	Mo(1)	+2.465	O(2)	−0.748	Mo(1)–O(2)	0.371
		Mo(1)–O(3)	1.78	H(4)	+0.524	O(3)	−1.008	Mo(1)–O(3)	−0.025
		O(3)–H(4)	0.96					O(3)–H(4)	0.498
	C4	Mo(1)–O(2)	1.86	Mo(1)	+3.508	O(2)	−1.148	Mo(1)–O(2)	−0.018
		O(2)–H(3)	0.96	H(3)	+0.564			O(2)–H(3)	0.528
	CX	Mo(1)–O(2)	1.68	Mo(1)	+2.647	O(2)	−0.738	Mo(1)–O(2)	0.286
		Mo(1)–O(3)	1.99	H(4)	+0.491	O(3)	−1.091	Mo(1)–O(3)	0.104
		O(3)–H(4)	0.96			$O(H_2)$	−1.111	O(3)–H(4)	0.506
		$Mo(1)–OH_2$	2.39					$Mo(1)–OH_2$	−0.034

value means an anti-bonding character. The bond order for the A1 cluster is large positive (0.259) for the Mo–O bond, as shown in Table 1, which implies that the Mo–O bonds of the species A1 are strong.

We next examined another cluster model, A2 with an O_h center. In this case, the OH distance was kept constant at 0.96 Å, and the distances of the two kinds of Mo–O bonds were optimized. As can be seen in A2 of Fig. 2, the shape of the observed spectrum and that of the reproduced one using the A2 cluster are not very much different; however, the bond orders of the Mo–O bonds obtained for cluster A2 are largely negative (−0.456 and −0.874), which implies that the Mo–O bonds have an anti-bonding character. Thus, the cluster is very weakly combined in it through such covalent bonds, even if it exists. As a result, it has been proposed that the molybdate ion exists as a T_d ion, not as an O_h ion, as is already known.

In order to investigate the effect of hydration, the cluster model shown as A3 in Fig. 1 was examined. As the hydrogen-bond length (Mo)O–H–O(H), 2.85 Å was used.[19] The reproduced spectrum using this cluster was again fitted to the observed spectrum when the Mo–O bond length was 1.80 Å. Here, all of the peak intensities used to reproduce spectrum A3 in Fig. 2 were set to be the same because the calculation of the dipole transition probability did not converge in this case. To simplify successive calculations, we determined the optimum structure model by adjusting the Mo–O bond lengths without taking the hydration sphere into account.

Cluster Model of $HMoO_4^-$ Giving the Best Fit to UV-vis Spectrum. In Fig. 4, the obtained component spectrum of the hydrogenmolybdate ion, $HMoO_4^-$, the result of the peak separation, and the spectra obtained by an MO calculation assuming B1, B3, and B4 clusters of Fig. 1 are shown. In any cluster the O–H distance was kept constant (0.96 Å), and the Mo–O distances were optimized. Even in this case, the bond order of the Mo(1)–O(3) bond, assuming that an O_h-centered cluster (B4) becomes very negative (−0.174), implying that the hydrogenmolybdate ion is not an O_h-centered type. B1, B2, and B3 are clusters having a T_d center. B1 has a straight Mo–O–H bond. In B2 and

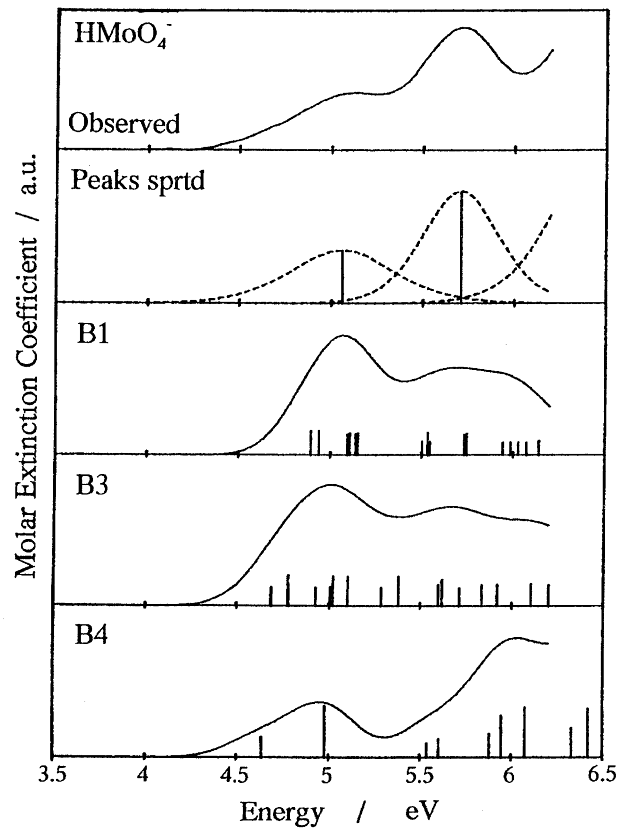

Fig. 4. First panel: component spectrum of hydrogenmolybdate ion $HMoO_4^-$; the second panel: result of peak separation; and the spectra reproduced from DV-$X\alpha$-MO calculation using the cluster models, B1, B3, and B4.

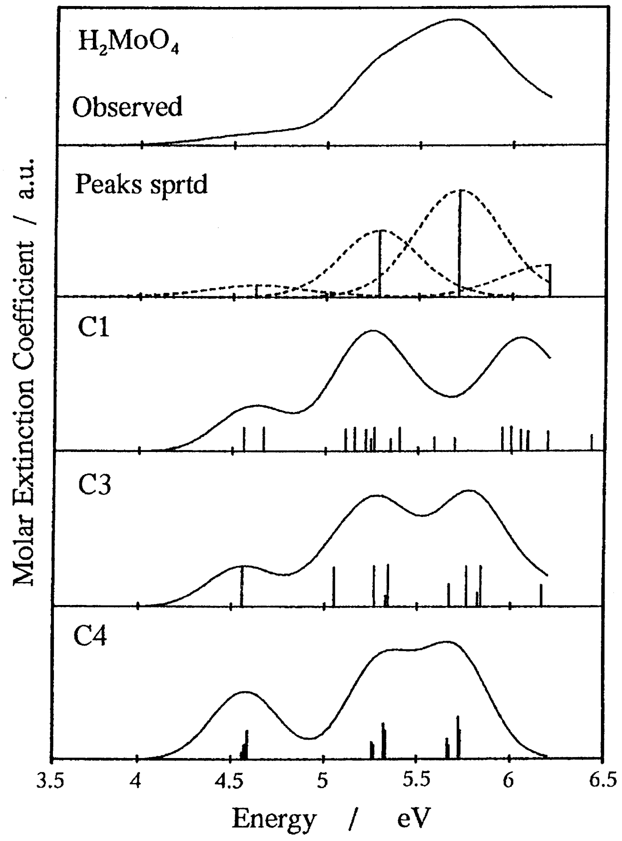

Fig. 5. First panel: component spectrum of dihydrogen molybdate H_2MoO_4; the second panel: result of peak separation; and the spectra reproduced from DV-$X\alpha$-MO calculation using the cluster models, C1, C3, and C4.

B3, the Mo–O–H bond is bent; the angle of Mo–O–H is 109°28′, the ideal tetrahedral angle. In the B2 cluster, the hydrogen atom exists just over another Mo–O bond at the bottom plane; however, in the B3 cluster, the hydrogen atom exists over the intermediate position of the two bottom Mo–O bonds. The peak separation of the observed spectrum gave three peaks; a comparison of the observed spectrum with the spectrum reproduced from the MO calculation may suggest that the B3 cluster is the preferable one. The bond order has large positive values (0.321, 0.189, 0.533) at this cluster. We would now like to propose that the $HMoO_4^-$ ion is a T_d-centered species, probably close to the B3 cluster of Fig. 1, even though free rotation around the Mo–O(H) axis can be expected.

Cluster Model of H_2MoO_4 Giving the Best Fit to UV-vis Spectrum. In Fig. 5, the obtained component spectrum of the dihydrogen molybdate species, H_2MoO_4, the result of peak separation, and the spectra obtained by an MO calculation assuming the C1, C3, and C4 clusters of Fig. 1 are shown. In any cluster, the O–H distance was kept constant at 0.96 Å, and the Mo–O distances were optimized. In this case, the discrepancy between the observed spectrum and that reproduced assuming an O_h-centered cluster C4 is not large. Also, T_d-centered clusters C2 and C3 gave similar spectra. In this case, all of the clusters gave very small values for the bond orders of the Mo–OH bonds; some of them were negative. There is a possibility that this species, H_2MoO_4, exists as an intermediate structure between the T_d-centered one and the O_h-centered one. Thus, the structure model CX shown in Fig. 6 was examined. Suppose that two water molecules come to close an H_2MoO_4 molecule with a T_d-centered cluster C3, as shown in the first panel of Fig. 6; it then leads a species CX. If hydrogen atoms are moving from a position next to one oxygen atom to a position next to another oxygen atom, and if its movement is very fast, the cluster model may be considered as C4, shown in the bottom panel of Fig. 6. In other words, the CX cluster is an intermediate form between the C3 structure and the C4 structure. The CX structure has many coordination parameters; we examined many of them. The cluster model shown here is that giving the best fit to the observed spectrum among those examined.

In Fig. 7, the reproduced spectra using C3, C4, and CX are compared. Each of them basically consists of three peaks, and gives a fair agreement to the observed spectrum. However, when the CX cluster was used, the bond order between the Mo–O atoms all became positive, except for those between the center Mo and the oxygen of the hydrating water molecule. This negative value is also not large. A kind of distorted octahedral structure, such as CX should be taken into account as a candidate of a dissolved structure model of

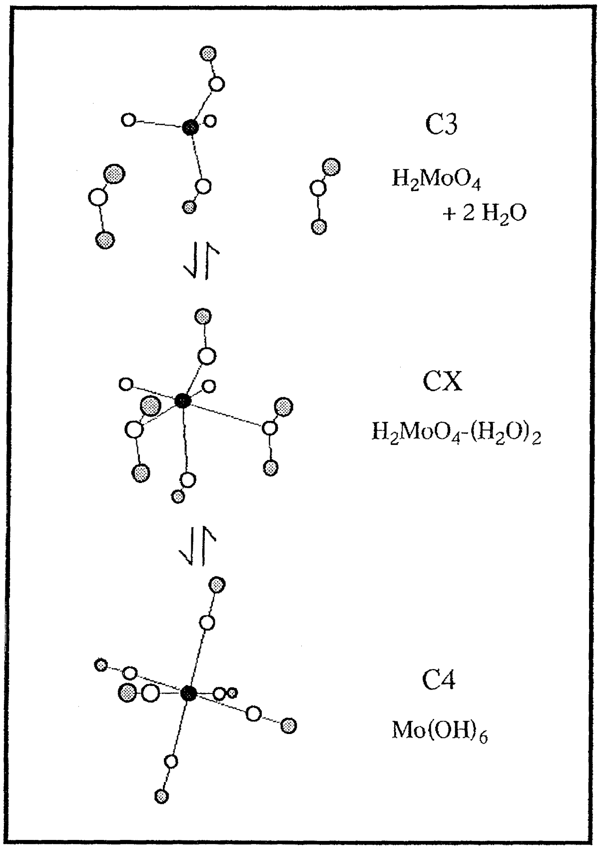

Fig. 6. Illustration of hypothetical structure change reaction of the dihydrogen molybdate H_2MoO_4.

H_2MoO_4 in solution.

From an acidified solution of the molybdate salt, a white crystal of H_2MoO_4, 'white α molybdic acid',[20] can be easily isolated. The bond lengths in this crystal have been reported to be Mo–O (terminal) 1.688, 1.687 Å, Mo–O (bridge) 2.277, 1.959, 1.949 Å, and Mo–H_2O 2.346 Å.[20] Similarly, in the crystal of $HgMoO_4$, which is considered to contain distorted octahedral Mo units, the Mo–O bonds have been reported to be 1.72, 1.94, 2.33 Å.[21] The CX structure proposed by this study consists of three similar kinds of Mo–O bonds: 1.68, 1.99, and 2.38 Å. A structure described as $MoO_2(OH)_2(OH_2)_2$ has been proposed by Tytko[22] and by Cruywagen et al.[23] for the solution system, recently.

Interpretation of the Condensation Reactivity of the Molybdate Ion. As can be seen from the above discussion, the bond order is a measure of the strength of the covalent character. The bigger is the bond order, the stronger is the covalent character, and it is also supposed that the more stable is the species. Thus, the value of the bond order can be used as a kind of criterion to justify the possibility of a reaction. In a previous paper[13] the preference of the dimerization reaction of hydrogenchromate $HCrO_4^-$ to form its dimer, $Cr_2O_7^{2-}$, was ascribed to the weak bond of Cr–O-(H) in $HCrO_4^-$. Although the Cr–OH bond of $HCrO_4^-$ is weak, the Cr–OCr bond of $Cr_2O_7^{2-}$ is strong; thus, $HCrO_4^-$ may breaks its Cr–OH bond and forms a dichromate ion

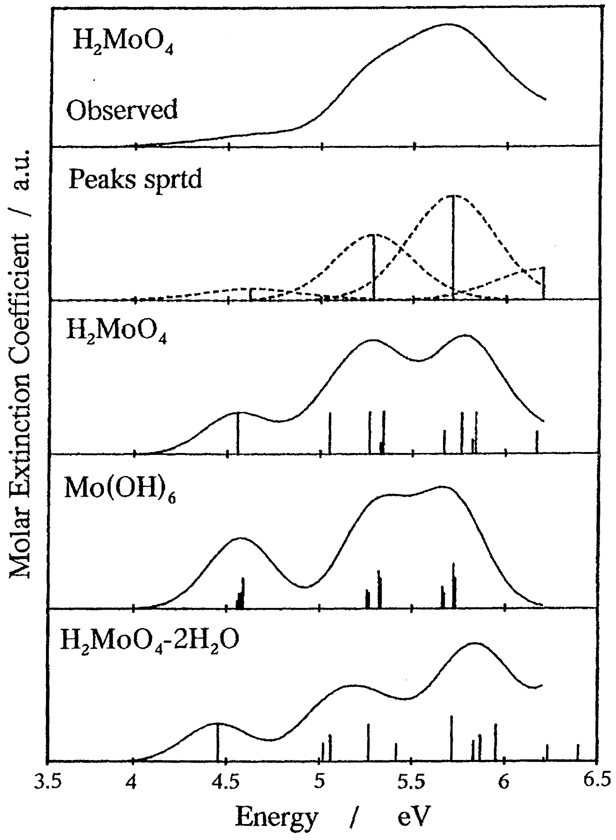

Fig. 7. First panel: component spectrum of dihydrogen molybdate H_2MoO_4; the second panel: result of peak separation; and the spectra reproduced from DV-$X\alpha$-MO calculation using the cluster models, C3, C4, and CX (of Fig. 6).

$Cr_2O_7^{2-}$ with another $HCrO_4^-$ ion.

In the case of the molybdate ion, the bond order of Mo–OH of the dihydrogen molybdate species, H_2MoO_4 (Mo(1)–O(3) in the C1, C2, C3: 0.033 to −0.025), is rather smaller, almost by one order, than that of the hydrogenmolybdate $HMoO_4^-$ (Mo(1)–O(3) in B3: 0.189). Namely, although the Mo–OH bond of $HMoO_4^-$ is strong, that of H_2MoO_4 is very weak.

Here, the following three dimerization reactions are considered:

$$HMoO_4^- + HMoO_4^- = MoO_4^-\text{–}H + HO\text{–}MoO_3^- = Mo_2O_7^{2-} + H_2O \qquad (5)$$

$$HMoO_4^- + H_2MoO_4 = MoO_4^-\text{–}H + HO\text{–}MoO_3H = HMo_2O_7^- + H_2O \qquad (6)$$

$$H_2MoO_4 + H_2MoO_4 = HMoO_4\text{–}H + HO\text{–}MoO_3H = H_2Mo_2O_7 + H_2O \qquad (7)$$

We assume that the structures of $Mo_2O_7^{2-}$, $HMo_2O_7^-$, and $H_2Mo_2O_7$ are D1, D2, and D3 of Fig. 1, respectively. Since H_2MoO_4 has a weak Mo–OH bond, the reactions of Eqs. 6 and 7 are favorable; however, the reaction of Eq. 5 is less favorable. Thus, the existence of $HMo_2O_7^-$ (Eq. 6) and that of $H_2Mo_2O_7$ (Eq. 7) can be expected.

So far, the presence of an isolated dimer anion, $Mo_2O_7{}^{2-}$, which comprises two MoO_4 tetrahedra sharing corner O atoms, has not been reported for a solution system, except for the $MgMo_2O_7$ crystal.[24] On the other hand, Cruywagen has proposed the existence of a dimeric anion $HMo_2O_7{}^-$ to explain their potentiometric data;[6,10] Tytko et al. have proposed that small aggregates, such as $HMo_2O_7{}^-$, trimer, and tetramer, would exist in low concentration solutions of molybdenum(VI).[9] Their propositions agree with our expectation.

The preference of dimerization reactions Eqs. 6 and 7 proposes that the H_2MoO_4 species plays an important role in the reactions. Cruywagen et al.[5] have suggested that the formation of the isopolymolybdate ion occurs according to the following reaction:

$$Mo(OH)_6 + xHMoO_4{}^- = [MoO_x(OH)_{6-x}(MoO_3)_x]^{x-} + xH_2O \quad (8)$$

The first step in this reaction is essentially the same as that in Eq. 6 because H_2MoO_4 and $Mo(OH)_6$ are interchangeable, as shown in Fig. 6. According to Cruywagen's argument concerning this condensation reaction (Eq. 8), much more tetrahedral molybdates ($HMoO_4{}^-$) can be linked by sharing a weak corner of the central molybdate ($Mo(OH)_6$ in place of H_2MoO_4). And, when six tetrahedra have been accommodated, all of these peripheral tetrahedra can expand to octahedra simply by folding at the common corners to share the octahedral edges along with a considerable decrease in enthalpy. This negative enthalpy change can be expected to stabilize the resultant product ion, heptamer $Mo_7O_{24}{}^{6-}$.[5]

On the other hand, the neutral dimer, $H_2Mo_2O_7$, formed by the reaction in Eq. 7 may follow succeeding condensation reactions, because the bond of Mo–OH in H_2MoO_4 is very weak. Thus, the following reaction can be expected:

$$\begin{aligned} &H_2Mo_2O_7 + xH_2MoO_4 \\ &\quad = HO_3MoOMoO_2O\text{–}H + xHO\text{–}MoO_3H \\ &\quad = HO_3MoOMoO_3MoO_3 \cdots MoO_3H + xH_2O \quad (9) \end{aligned}$$

In this case, there is no limit to the amount of aggregation (x), because the product is a neutral species. It is well known that a white crystal of H_2MoO_4, called 'white α molybdic acid', can be easily precipitated from an acidified solution.[20] This fact may imply that species having various degrees of condensation exist in a solution of relatively low molybdate concentration. The degree of condensation (x) should depend on the concentration of the total molybdate ion. Then, a number of equilibrium constants corresponding to various x values have to be taken into account to explain the net equilibria in such a solution. This may be the reason why the solution equilibria of the molybdate solution of pH region 1—3 have been very confused so far.[6,7,9]

Conclusions

The dissolved structure of the mononuclear molybdate species were estimated by fitting the component UV-vis spectrum with the spectrum reproduced by the DV-$X\alpha$ molecular orbital calculation. The degree of the fit between the two spectra and the bond order of the cluster model were used to choose the optimum dissolved structure. The bond order values were used to interpret the possible condensation reactions of the mononuclear molybdate species.

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