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Quantum chemical calculations on structure of $Mo_8O_{26}^{4-}$ ①

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[Abstract] Two possible structures of $Mo_8O_{26}^{4-}$ were optimized using the Polak-Ribiere method of Molecular Mechanics Optimization and the termination condition is RMS (Root-mean-square) gradient of 0.42 kJ/mol. Based on the calculations of the molecular dynamics, Lengevin dynamics and Monte Carlo dynamics simulation, the structure models of $Mo_8O_{26}^{4-}$ with the lowest energy were acquired respectively according to the energy of the systems calculated using the ZINDO/1 and PM3 methods. The total energy, energies of some frontier molecular orbitals and atomic charges of $Mo_8O_{26}^{4-}$ were computed at the HF/3-21G and HF/STO-3G levels. The calculation results show that the contortion of the structure with eight MoO_6 is smaller than that of the structure with six MoO_6 and two MoO_4. The total energies of the two structures are nearly equal because the contortion of the structure with six MoO_6 and two MoO_4 would make the exclusion force decreased.

[Key words] quantum chemistry calculation; $Mo_8O_{26}^{4-}$; structure
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1 INTRODUCTION

Ammonium molybdate $(NH_4)_4Mo_8O_{26}$ is a main industrial raw material for the production of molybdenum powder at present. Some properties of ammonium molybdates such as their thermal decompositions and applications in some certain fields, etc, have been studied in detail; while the structure of ammonium molybdate was less involved.[1~10]

As a kind of isopolyoxometallate, the structure of ammonium molybdate $(NH_4)_4Mo_8O_{26}$ is dependent on the structure of isopolyanion $Mo_8O_{26}^{4-}$. Any molybdenum isopolyanion is made up of MoO_6 octahedrons in theory and some of the MoO_6 octahedrons share the edges of MoO_6 at any rate[11, 12]. It is known that the charge of positive ion Mo^{6+} is very high, so the exclude force among the positive ions is rather large. If the positive ion Mo^{6+} could move in MoO_6 octahedron the exclusive force may be decreased. That is to say, the contortion of the MoO_6 octahedron may lead to the stabilization from view of energy.[12] According to the stable heaping mode of edge sharing of multi-octahedron[12], there are two possible structures of $Mo_8O_{26}^{4-}$, as shown in Fig. 1, to keep the ratio of $n(Mo):n(O) = 4:13$. The possible structure (a) is made up of eight MoO_6 octahedrons with Mo—Mo—Mo bond angle of 90°, which has the lowest exclusive force theoretically.[12] The possible structure (b) is made up of six MoO_6 octahedrons and two MoO_4 tetrahedrons where the six MoO_6 octahedrons are heaped with Mo—Mo—Mo bond angle of 120° and 90° to form ring. There exists one MoO_4 tetrahedron respectively upside and downside. The exclusive force of the structure (b) is larger than that of structure (a) in theory.[12]

The two possible structures of $Mo_8O_{26}^{4-}$ were studied by quantum chemistry calculation method in this paper.

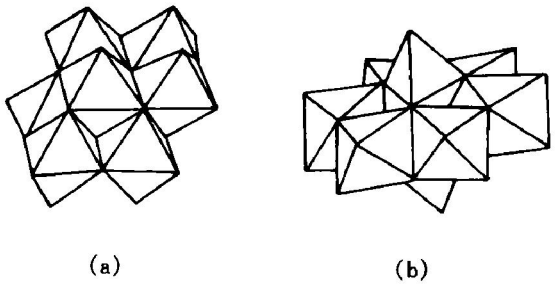

Fig. 1 Two possible structures of $Mo_8O_{26}^{4-}$
(a) —Structure (a); (b) —Structure (b)

2 GEOMETRICAL OPTIMIZATION OF CALCULATION MODEL OF $Mo_8O_{26}^{4-}$

The two different structures of $Mo_8O_{26}^{4-}$ were optimized using the Polak-Ribiere method of Molecular Mechanics Optimization and the termination condition is RMS (Root-mean-square) gradient of 0.42 kJ/mol. The molecular dynamics, Lengevin dynamics and Monte Carlo dynamics simulation were proceeded and the energy of every system was calculated using the ZNDO/1 and PM3 methods respectively. The calculation results are shown in Table 1. From Table 1, the two structure models of $Mo_8O_{26}^{4-}$ with the lowest energy are chosen as structure (a)-Opt and structure (b)-Opt, are shown in Fig. 2 and Fig. 3. The calculation results of bond length and bond angle of

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the structures (a)-Opt and (b)-Opt are presented in Table 2~ 5.

It can be seen from Table 2 that the angle degrees among eight molybdenum atoms are all about 90° which means that MoO_6 octahedrons of the structure (a)-Opt are heaped with the steady mode[12].

Table 1 Calculation results of geometrical optimization models of $Mo_8O_{26}^{4-}$ using PM3 and ZIDO/1 methods

Structure of $Mo_8O_{26}^{4-}$	Method of geometry optimization	Calculation method	Calculation results/(kJ·mol^{-1}) Total energy	Binding energy	Heat of formation	Electronic energy	Nuclear energy
(a)-Opt	Molecular mechanics optimization	ZIDO/1	9 273.6	83 865.7	84 537.2	− 397 853.3	407 126.8
		PM3	− 3 515.8	49 104.5	49 776.0	− 394 956.2	391 440.2
	Molecular dynamics simulation	ZIDO/1	− 37 290.6	37 301.4	37 972.9	− 444 472.7	407 182.1
		PM3	− 14 033.0	38 587.2	39 258.8	− 405 524.4	391 491.4
	Langevin dynamics simulation	ZIDO/1	− 24 168.2	50 423.8	51 095.3	− 431 300.9	407 132.8
		PM3	− 4 665.6	47 954.7	48 626.2	− 396 111.5	391 445.9
	Monte Carlo simulation	ZIDO/1	− 37 269.5	37 322.6	37 994.1	− 444 388.3	407 118.7
		PM3	− 923.5	51 696.8	52 368.3	− 392 356.5	391 433.0
(b)-Opt	Molecular mechanics optimization	ZIDO/1	10 553.1	85 125.0	85 796.6	− 373 735.6	384 268.7
		PM3	28 406.3	81 026.7	81 698.2	− 341 680.6	370 087.1
	Molecular dynamics simulation	ZIDO/1	12 452.0	87 044.0	87 715.6	− 374 905.7	387 357.7
		PM3	− 52 838.4	− 218.0	435.3	− 425 891.9	373 053.3
	Langevin dynamics simulation	ZIDO/1	9 884.7	84 476.7	85 148.3	− 377 483.0	387 367.7
		PM3	24 123.9	76 744.2	77 415.7	− 348 939.2	373 063.2
	Monte Carlo simulation	ZIDO/1	− 19 052.8	55 538.2	56 210.7	− 406 530.6	387 477.8
		PM3	− 52 705.8	− 85.5	586.0	− 425 871.8	373 166.0

Table 2 Calculation results of bond angle of structure (a)-Opt (°)

$\angle O_6Mo_4O_1$	89.003 4	$\angle O_{14}Mo_{11}O_2$	90.625 8	$\angle O_{18}Mo_{16}O_3$	97.557 0	$\angle O_{28}Mo_{27}O_{25}$	88.786 7
$\angle O_6Mo_4O_2$	93.813 6	$\angle O_{14}Mo_{11}O_{10}$	90.042 3	$\angle O_{18}Mo_{16}O_5$	102.223 0	$\angle O_{28}Mo_{27}O_7$	95.240 6
$\angle O_6Mo_4O_5$	97.951 9	$\angle O_{14}Mo_{11}O_{12}$	90.828 5	$\angle O_{18}Mo_{16}O_{17}$	97.606 6	$\angle O_{28}Mo_{27}O_{19}$	97.689 4
$\angle O_6Mo_4O_3$	95.081 0	$\angle O_{14}Mo_{11}O_5$	81.381 4	$\angle O_{18}Mo_{16}O_{15}$	89.103 7	$\angle O_{28}Mo_{27}O_{26}$	93.733 5
$\angle O_7Mo_4O_1$	91.347 9	$\angle O_{13}Mo_{11}O_2$	89.129 8	$\angle O_{19}Mo_{16}O_3$	82.673 4	$\angle O_3Mo_{27}O_{25}$	91.856 1
$\angle O_7Mo_4O_2$	93.313 2	$\angle O_{13}Mo_{11}O_{10}$	90.081 0	$\angle O_{19}Mo_{16}O_5$	86.456 5	$\angle O_3Mo_{27}O_7$	77.783 8
$\angle O_7Mo_4O_5$	81.869 7	$\angle O_{13}Mo_{11}O_{12}$	89.409 9	$\angle O_{19}Mo_{16}O_{17}$	82.669 2	$\angle O_3Mo_{27}O_{19}$	81.812 6
$\angle O_7Mo_4O_3$	77.784 1	$\angle O_{13}Mo_{11}O_5$	98.495 1	$\angle O_{19}Mo_{16}O_{15}$	82.216 9	$\angle O_3Mo_{27}O_{26}$	93.217 7
$\angle O_6Mo_4O_7$	172.865 0	$\angle O_{13}Mo_{11}O_{14}$	179.729 0	$\angle O_{18}Mo_{16}O_{19}$	171.321 0	$\angle O_3Mo\ 27O_{28}$	173.018 0
$\angle O_5Mo_{29}O_7$	82.751 7	$\angle O_{33}Mo_{31}O_5$	98.030 5	$\angle O_{15}Mo_{24}O_{19}$	81.691 3	$\angle O_{17}Mo_{21}O_{19}$	81.809 0
$\angle O_5Mo_{29}O_{14}$	81.887 8	$\angle O_{33}Mo_{31}O_{12}$	93.292 6	$\angle O_{15}Mo_{24}O_{26}$	90.715 3	$\angle O_{17}Mo_{21}O_{34}$	77.775 9
$\angle O_5Mo_{29}O_{34}$	82.704 3	$\angle O_{33}Mo_{31}O_{32}$	89.195 7	$\angle O_{15}Mo_{24}O_{23}$	89.278 4	$\angle O_{17}Mo_{21}O_{22}$	92.106 2
$\angle O_5Mo_{29}O_{19}$	86.412 9	$\angle O_{33}Mo_{31}O_{17}$	94.868 2	$\angle O_{15}Mo_{24}O_{20}$	90.873 2	$\angle O_{17}Mo_{21}O_{20}$	93.396 8
$\angle O_{30}Mo_{29}O_7$	97.630 4	$\angle O_{34}Mo_{31}O_5$	81.836 2	$\angle O_8Mo_{24}O_{19}$	99.097 9	$\angle O_9Mo_{21}O_{19}$	97.109 8
$\angle O_{30}Mo_{29}O_{19}$	102.366 0	$\angle O_{34}Mo_{31}O_{12}$	94.060 4	$\angle O_8Mo_{24}O_{26}$	89.222 5	$\angle O_9Mo_{21}O_{34}$	95.504 0
$\angle O_{30}Mo_{29}O_{34}$	97.426 3	$\angle O_{34}Mo_{31}O_{32}$	91.100 9	$\angle O_8Mo_{24}O_{23}$	89.932 0	$\angle O_9Mo_{21}O_{22}$	89.107 8
$\angle O_{30}Mo_{29}O_{14}$	89.332 7	$\angle O_{34}Mo_{31}O_{17}$	77.773 3	$\angle O_8Mo_{24}O_{20}$	89.230 0	$\angle O_9Mo_{21}O_{20}$	93.266 8
$\angle O_{30}Mo_{29}O_5$	171.220 0	$\angle O_{34}Mo_{31}O_{33}$	172.641 0	$\angle O_8Mo_{24}O_{15}$	179.206 0	$\angle O_{17}Mo_{21}O_9$	173.223 0
$\angle Mo_4Mo_{11}Mo_{31}$	89.995 7	$\angle Mo_{24}Mo_{21}Mo_{29}$	90.079 0	$\angle Mo_{11}O_5Mo_{16}$	169.320 0	$\angle Mo_{29}O_{19}Mo_{24}$	169.694 0
$\angle Mo_4Mo_{16}Mo_{31}$	89.908 5	$\angle Mo_{21}Mo_{29}Mo_{27}$	89.875 2	$\angle Mo_4O_5Mo_{31}$	167.519 0	$\angle Mo_{27}O_{19}Mo_{24}$	89.394 2
$\angle Mo_{11}Mo_{31}Mo_{16}$	90.049 5	$\angle Mo_{11}Mo_4Mo_{16}$	90.107 7	$\angle Mo_4O_3Mo_{16}$	92.812 9	$\angle Mo_{27}O_{26}Mo_{24}$	92.747 7
$\angle Mo_{29}Mo_{27}Mo_{24}$	90.116 6	$\angle Mo_{11}O_5Mo_{31}$	89.315 1	$\angle Mo_4O_5Mo_{16}$	89.498 9	$\angle Mo_{29}O_{34}Mo_{21}$	92.830 6
$\angle Mo_{27}Mo_{24}Mo_{21}$	89.882 6	$\angle Mo_{11}O_{12}Mo_{31}$	92.665 7	$\angle Mo_{27}O_{19}Mo_{21}$	167.385 0	$\angle Mo_{29}O_{19}Mo_{21}$	89.492 9

Table 3 Calculatiom results of bond length of structure (a)-Opt (Å)

	Molybdenum-terminal oxygen Mo—O_a bond		Molybdenum-bridged oxygen Mo—O_b bond		Molybdenum-tri-bridged oxygen Mo—O_c bond		Molybdenum-central oxygen Mo—O_d bond	
	Mo_{11}—O_{13}	1.9671	Mo_{11}—O_2	1.9549	Mo_{31}—O_{17}	1.9567	Mo_{11}—O_5	2.0112
	Mo_{11}—O_{10}	1.9666	Mo_4—O_2	1.9542	Mo_{16}—O_{17}	1.9513	Mo_4—O_5	2.0118
	Mo_4—O_1	1.9670	Mo_{11}—O_{12}	1.9547	Mo_{21}—O_{17}	1.9661	Mo_{16}—O_5	2.0118
	Mo_{16}—O_{18}	1.9640	Mo_{31}—O_{12}	1.9540	Mo_{31}—O_{34}	1.9660	Mo_{31}—O_5	2.0114
	Mo_{27}—O_{25}	1.9666	Mo_{16}—O_{15}	1.9627	Mo_{29}—O_{34}	1.9512	Mo_{29}—O_5	1.9920
	Mo_{27}—O_{28}	1.9655	Mo_{24}—O_{15}	1.9635	Mo_{21}—O_{34}	1.9566	Mo_{16}—O_{19}	1.9918
	Mo_{29}—O_{30}	1.9643	Mo_{21}—O_{23}	1.9542	Mo_4—O_7	1.9661	Mo_{29}—O_{19}	2.0099
	Mo_{24}—O_8	1.9667	Mo_{24}—O_{20}	1.9549	Mo_{29}—O_7	1.9511	Mo_{27}—O_{19}	2.0111
	Mo_{24}—O_{23}	1.9667	Mo_{24}—O_{26}	1.9549	Mo_{27}—O_7	1.9565	Mo_{24}—O_{19}	2.0117
	Mo_{21}—O_9	1.9655	Mo_{27}—O_{26}	1.9540			Mo_{16}—O_{19}	2.0110
	Mo_{21}—O_{22}	1.9665	Mo_{29}—O_{14}	1.9633				
	Mo_{31}—O_{32}	1.9668	Mo_{11}—O_{14}	1.9641				
	Mo_{31}—O_{33}	1.9655						
Average		1.9659		1.9574		1.9579		2.0073

Table 4 Calculation results of bond angle of structure (b)-Opt (°)

$\angle O_5Mo_3O_1$	71.840 0	$\angle O_8Mo_9O_6$	82.634 9	$\angle O_{13}Mo_{12}O_{34}$	107.046 0	$\angle O_{21}Mo_{24}O_{22}$	68.655 9
$\angle O_5Mo_3O_{23}$	109.785 0	$\angle O_8Mo_9O_7$	103.633 0	$\angle O_{13}Mo_{12}O_{30}$	90.078 8	$\angle O_1Mo_{24}O_6$	84.619 9
$\angle O_5Mo_3O_2$	96.477 8	$\angle O_8Mo_9O_{10}$	124.997 0	$\angle O_{13}Mo_{12}O_6$	96.351 6	$\angle O_{21}Mo_{24}O_{23}$	87.284 0
$\angle O_5Mo_3O_4$	88.610 2	$\angle O_8Mo_9O_5$	81.838 5	$\angle O_{13}Mo_{12}O_{11}$	91.828 7	$\angle O_{21}Mo_{24}O_{27}$	117.045 0
$\angle O_{27}Mo_3O_1$	88.069 8	$\angle O_1Mo_9O_7$	67.974 2	$\angle O_7Mo_{12}O_{30}$	82.904 0	$\angle O_{22}Mo_{24}O_{25}$	90.924 8
$\angle O_{27}Mo_3O_{23}$	73.873 3	$\angle O_1Mo_9O_6$	135.065 0	$\angle O_7Mo_{12}O_6$	70.803 8	$\angle O_{26}Mo_{24}O_{25}$	83.988 6
$\angle O_{27}Mo_3O_4$	87.074 3	$\angle O_1Mo_9O_{10}$	101.904 0	$\angle O_7Mo_{12}O_{30}$	100.809 0	$\angle O_{23}Mo_{24}O_{25}$	120.089 0
$\angle O_{27}Mo_3O_2$	104.256 0	$\angle O_1Mo_9O_5$	71.694 7	$\angle O_7Mo_{12}O_{34}$	87.095 9	$\angle O_{27}Mo_{24}O_{25}$	84.323 6
$\angle O_{27}Mo_3O_5$	158.960 0	$\angle O_1Mo_9O_8$	123.585 0	$\angle O_7Mo_{12}O_{13}$	161.661 0	$\angle O_{21}Mo_{24}O_{25}$	150.192 0
$\angle O_{21}Mo_{17}O_{18}$	116.133 0	$\angle O_{32}Mo_{31}O_{16}$	133.834 0	$\angle O_{30}Mo_{28}O_{16}$	89.061 1	$\angle O_{20}Mo_{19}O_{21}$	120.593 0
$\angle O_{21}Mo_{17}O_{22}$	68.809 5	$\angle O_{32}Mo_{31}O_{33}$	83.147 8	$\angle O_{29}Mo_{28}O_{16}$	122.113 0	$\angle O_{20}Mo_{19}O_1$	121.308 0
$\angle O_{21}Mo_{17}O_{16}$	143.485 0	$\angle O_{32}Mo_{31}O_{34}$	86.588 3	$\angle O_7Mo_{28}O_{29}$	121.661 0	$\angle O_{21}Mo_{19}O_1$	111.020 0
$\angle O_{21}Mo_{17}O_{14}$	81.280 5	$\angle O_{32}Mo_{31}O_{14}$	85.666 5	$\angle O_{30}Mo_{28}O_{29}$	114.973 0	$\angle O_{23}Mo_{19}O_1$	87.926 0
$\angle O_{15}Mo_{17}O_{16}$	87.615 2	$\angle O_{16}Mo_{31}O_{33}$	85.709 0	$\angle O_7Mo_{28}O_{16}$	111.765 0	$\angle O_{23}Mo_{19}O_{20}$	115.790 0
$\angle O_{15}Mo_{17}O_{14}$	87.417 0	$\angle O_{16}Mo_{31}O_{14}$	72.630 3	$\angle O_{30}Mo_{28}O_7$	84.926 5	$\angle O_{23}Mo_{19}O_{21}$	90.835 2
$\angle O_{15}Mo_{17}O_{18}$	108.047 0	$\angle O_{16}Mo_{31}O_{30}$	85.707 3				
$\angle O_{15}Mo_{17}O_{22}$	83.718 9	$\angle O_{16}Mo_{31}O_{34}$	130.491 0				
$\angle O_{15}Mo_{17}O_{21}$	117.018 0	$\angle O_{32}Mo_{31}O_{30}$	137.407 0				

Table 5 Calculation results of bond length of structure (b)-Opt (Å)

	Molybdenum-terminal oxygen Mo—O_a bond		Molybdenum-bridged oxygen Mo—O_b bond		Molybdenum-tri-bridged oxygen Mo—O_c bond	
	Mo_{12}—O_{13}	1.964 4	Mo_{12}—O_6	1.983 7	Mo_{12}—O_{30}	1.991 5
	Mo_{12}—O_{11}	1.966 4	Mo_9—O_6	1.988 9	Mo_{28}—O_{30}	1.932 7
	Mo_9—O_8	1.968 0	Mo_{12}—O_{34}	1.976 3	Mo_{31}—O_{30}	2.003 4
	Mo_9—O_{10}	1.965 8	Mo_{31}—O_{34}	1.977 9	Mo_{31}—O_{16}	1.993 5
	Mo_{19}—O_{20}	1.959 7	Mo_{31}—O_{16}	1.993 5	Mo_{28}—O_{16}	1.943 7
	Mo_{31}—O_{32}	1.968 7	Mo_{17}—O_{16}	1.978 3	Mo_{17}—O_{16}	1.978 3
	Mo_{31}—O_{33}	1.968 8	Mo_{31}—O_{14}	1.978 5	Mo_{17}—O_{21}	1.977 0
	Mo_{17}—O_{15}	1.967 9	Mo_{17}—O_{14}	1.980 4	Mo_{24}—O_{21}	1.997 5
	Mo_{17}—O_{18}	1.977 3	Mo_{17}—O_{22}	1.988 8	Mo_{19}—O_{21}	1.936 7
	Mo_{24}—O_{25}	1.967 9	Mo_{24}—O_{22}	1.976 1	Mo_{23}—O_{24}	1.997 9
	Mo_3—O_4	1.966 8	Mo_{24}—O_{27}	1.976 9	Mo_{19}—O_{23}	1.934 7
	Mo_3—O_2	1.964 3	Mo_3—O_{27}	1.975 7	Mo_9—O_1	1.969 2
			Mo_3—O_5	1.980 7	Mo_3—O_1	1.969 0
			Mo_5—O_9	1.987 5	Mo_{19}—O_1	1.950 4
Average		1.967 2		1.981 7		1.969 8

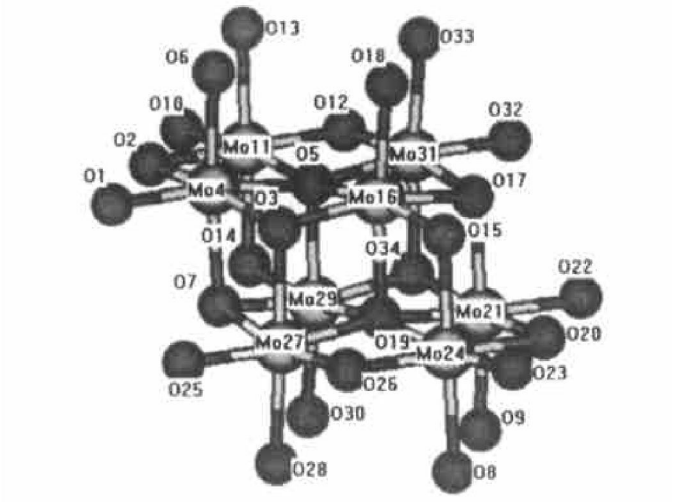

Fig. 2 Model of structure(a)-Opt

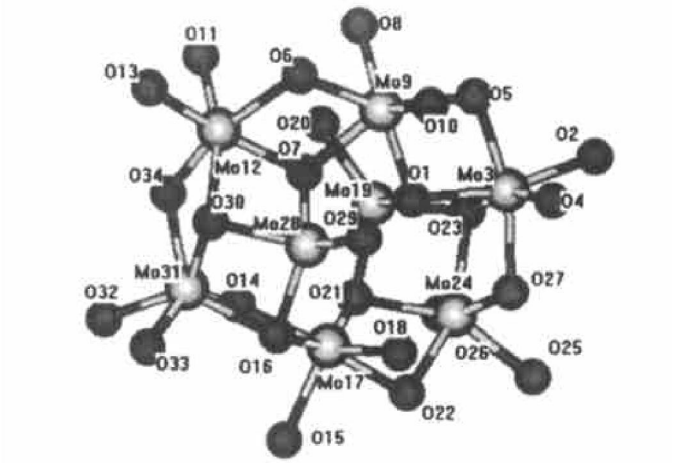

Fig. 3 Model of structure (b)-Opt

The bond angles of $\angle O_6Mo_4O_7$, $\angle O_{18}Mo_{16}O_{19}$, $\angle O_{30}Mo_{29}O_5$, $\angle O_{34}Mo_{31}O_{33}$, $\angle O_{17}Mo_{21}O_9$ and so on, are about 172°, $\angle O_{13}Mo_{11}O_5$, $\angle O_8Mo_{24}O_{19}$ and so on about 99°, $\angle O_3Mo_{27}O_7$, $\angle O_{34}Mo_{31}O_{17}$ and so on about 77°, which shows that the eight MoO_6 octahedrons are contorted to a certain extent.

According to the Ref. [11], the average bond length of the molybdenum-terminal oxygen Mo—O_a bond, molybdenum-bridge oxygen Mo—O_b bond and molybdenum-central oxygen Mo—O_d bond are 1.98, 1.97 and 2.28 Å respectively in $Mo_6O_{19}^{2-}$, which is heaped with six MoO_6 octahedrons. From Table 3, it can be seen that the average bond length of the molybdenum-terminal oxygen Mo—O_a bond, molybdenum-bridge oxygen Mo—O_b bond, molybdenum-tri-bridged oxygen Mo—O_c bond and molybdenum-central oxygen Mo—O_d are 1.965 9, 1.957 4, 1.957 9 and 2.007 3 Å respectively in the structure (a)-Opt $Mo_8O_{26}^{4-}$. The calculation results of bond length are accorded with the corresponding bond length in $Mo_6O_{19}^{2-}$, which means that the results of the geometrical optimized are reliable to some extent.

It is found from Table 4 that the six MoO_6 octahedrons and two MoO_4 tetrahedrons of the structure (b)-Opt are contorted obviously. Compared with the angles of 180° and 90° of the regular octahedron, the largest deviations are about 60° and 45°. Compared with the angle of 108° of the regular tetrahedron in the same way, the largest deviation is 20°. Therefore, the degree of contortion of the structure (b)-Opt is larger than that of the structure (a)-Opt.

From Table 5, it can be seen that the average bond length of the molybdenum-terminal oxygen Mo—O_a bond, molybdenum-bridge oxygen Mo—O_b bond and molybdenum-tri-bridged oxygen Mo—O_c bond are 1.967 2, 1.981 7 and 1.969 8 Å respectively in the structure (b)-Opt $Mo_8O_{26}^{4-}$. Meanwhile, the distribution of length of the molybdenum-tri-bridged oxygen Mo—O_c bond is not equal between 1.92 Å and 2.00 Å. Therefore, the polarity of the molybdenum-tri-bridged oxygen Mo—O_c bond is different. It is similar that the bond length of the molybdenum-terminal oxygen Mo—O_a bond and molybdenum-bridged oxygen Mo—O_b bond are accorded with the corresponding bond length of 1.98 Å and 1.97 Å in $Mo_6O_{19}^{2-}$ [11], which also indicates that the results of the geometrical optimization are reliable to a certain extent.

3 CALCULATION RESULTS AND DISCUSSION

3.1 Calculation methods

The total energy, some frontier molecular orbital energies and atomic charges of structure (a)-Opt (Fig. 2) and structure (b)-Opt were computed at the HF/3-21G and HF/STO-3G levels using Gaussian94 program. All calculations were performed at Cernis2 Work Station in Central South University.

3.2 Calculation energy

Total energies of the two structures of $Mo_8O_{26}^{4-}$ are shown in Table 6. It can be seen that the total energies of these two structures are almost equal. Therefore, the stability of these two structures is nearly the same. The calculation results are accorded with the results of geometrical optimization. Although the six MoO_6 octahedrons of the structure (b)-Opt are heaped with the Mo—Mo—Mo bond angles of 120° and 90° which is not the most stable mode of heaping, the contortion of the structure (b)-Opt may lead to the stabilization from view of energy.

Table 6 Calculation of total energy of two structures of $Mo_8O_{26}^{4-}$ ($\times 10^{-13}$ J)

Structure	STO-3G	3-21G
$Mo_8O_{26}^{4-}$ (a)-Opt	−1.456 434 3	−1.464 344 4
$Mo_8O_{26}^{4-}$ (b)-Opt	−1.456 430 5	−1.464 345 0

274 bonding molecular orbits and 274 antibonding molecular orbits were acquired using quantum chemistry calculation method. The 274th orbital is HOMO and the 275th is LUMO. The energies of some frontier molecular orbits of the two structures are listed in Table 7. It can be seen that the energy of HOMO of structure (b)-Opt is higher than that of the structure (a)-Opt and the energy of LUMO of the structure (b)-Opt is lower than that of the structure (a)-Opt. It is proclaimed that the spectrum features of these two structures should be different.

3.3 Calculations of atomic charge

The atomic charges of structures (a)-Opt and (b)-Opt are listed in Table 8 and Table 9. From Table 8 it can be seen that the charges of eight Mo of structure (a)-Opt are about 0.695 885~ 0.781 367 (STO-3G) and 1.213 642~ 1.402 782 (3-21G) and the charges of oxygen atoms are about - 0.130 511~ - 0.506 517(STO-3G) as well as - 0.189 983~ - 1.133 814 (3-21G). That is to say, number of attraction electron is not integer, so that the skeleton of $Mo_8O_{26}^{4-}$ are connected by covalence mainly. The charge distribution of oxygen atoms is not homogeneous on the whole; but the charges of the oxygen atoms in the same position are approximation, for example, O13 and O8, O33 and O28, O30 and O18, and so on, which are all the terminal oxygen atoms. From Table 9 it can be seen that the charges of the same oxygen atoms of the structures (b)-Opt are not approximation, for instance, O11 and O26, O13 and O25, O4 and O32, and so on, which are all the terminal oxygen atoms. It also shows that the degree of contortion of the structure (b)-Opt is larger than that of the structure (a)-Opt.

Table 7 Some energies of molecular orbitals of two structures of $Mo_8O_{26}^{4-}$

Occupied orbital energy ($\times 10^{-18}$J)					Virtual orbital energy ($\times 10^{-18}$J)				
Orbital number	Structure (a)-Opt		Structure (b)-Opt		Orbital number	Structure (a)-Opt		Structure (b)-Opt	
	STO-3G	3-21G	STO-3G	3-21G		STO-3G	3-21G	STO-3G	3-21G
274	1.275 82	0.104 20	1.362 84	0.175 00	275	2.182 47	0.964 98	1.936 23	0.758 59
273	1.263 35	0.086 71	1.310 00	0.135 85	276	2.204 66	0.982 85	1.967 53	0.863 13
272	1.228 21	0.061 95	1.279 79	0.065 61	277	2.253 01	1.048 99	2.344 86	0.947 45
271	1.224 81	0.049 31	1.273 60	0.025 55	278	2.290 72	1.085 96	2.399 01	1.633 34
270	1.069 57	0.027 81	1.240 51	- 0.015 56	279	2.335 19	1.150 52	2.401 72	1.160 25
269	1.029 76	0.008 46	1.150 79	- 0.033 09	280	2.345 61	1.165 09	2.454 42	1.197 26
268	1.009 79	- 0.030 69	1.116 34	- 0.049 44	281	2.584 65	1.361 84	2.459 66	1.281 10
267	0.999 55	- 0.051 01	1.107 80	- 0.073 50	282	2.584 65	1.381 81	2.496 41	1.333 68

Table 8 Atomic charges of structure (a)-Opt

No.	Atom	STO-3G	3-21G	No.	Atom	STO-3G	3-21G
1	O	- 0.274 966	- 0.351 848	18	O	- 0.131 651	- 0.180 498
2	O	- 0.436 730	- 0.638 144	19	O	- 0.507 331	- 1.133 536
3	O	- 0.438 461	- 0.791 496	20	O	- 0.436 539 0	- 0.641 478
4	Mo	0.703 787	1.257 559	21	Mo	0.704 134	1.263 427
5	O	- 0.506 517	- 1.133 814	22	O	- 0.279 576	- 0.343 009
6	O	- 0.386 103	- 0.399 204	23	O	- 0.390 993	- 0.459 417
7	O	- 0.438 149	- 0.788 808	24	Mo	0.695 885	1.213 642
8	O	- 0.374 410	- 0.436 989	25	O	- 0.275 572	- 0.340 536
9	O	- 0.384 501	- 0.399 215	26	O	- 0.436 708	- 0.640 576
10	O	- 0.400 196	- 0.448 538	27	Mo	0.703 621	1.255 809
11	Mo	0.698 513	1.216 644	28	O	- 0.386 225	- 0.397 889
12	O	- 0.436 141	- 0.638 211	29	Mo	0.781 367	1.402 782
13	O	- 0.372 544	- 0.435 494	30	O	- 0.130 511	- 0.189 983
14	O	- 0.405 744	- 0.577 175	31	Mo	0.702 120	1.264 484
15	O	- 0.402 668	- 0.574 949	32	O	- 0.274 504	- 0.352 201
16	Mo	0.779 666	1.399 734	33	O	- 0.384 683	- 0.401 769
17	O	- 0.438 886	- 0.790 683	34	O	- 0.438 784	- 0.788 619

Table 9 Atomic charges of structure (b)-Opt

No.	Atom	STO-3G	3-21G	No.	Atom	STO-3G	3-21G
1	O	- 0.462 161	0.863 413	18	O	- 0.368 844	- 0.424 324
2	O	- 0.478 428	- 0.536 332	19	Mo	0.644 185 Mo	1.434 876
3	Mo	0.761 613	1.309 498	20	O	- 0.387 477	- 0.134 991
4	O	- 0.360 367	- 0.379 718	21	O	- 0.418 995	- 0.733 466
5	O	- 0.453 905	- 0.698 189	22	O	- 0.395 306	- 0.640 382
6	O	- 0.456 359	- 0.689 812	23	O	- 0.434 570	- 0.731 132
7	O	- 0.478 617	- 0.906 851	24	Mo	0.805 935	1.217 551
8	O	- 0.426 317	- 0.438 671	25	O	- 0.165 891	- 0.363 806
9	Mo	0.756 736	1.292 073	26	O	- 0.228 728	- 0.565 924
10	O	- 0.426 522	- 0.440 453	27	O	- 0.374 999	- 0.693 440
11	O	- 0.367 691	- 0.419 347	28	Mo	0.679 192	1.310 594
12	Mo	0.756 083	1.346 583	29	O	- 0.394 168	- 0.281 169
13	O	- 0.477 378	- 0.519 018	30	O	- 0.421 928	- 0.746 783
14	O	- 0.421 488	- 0.713 582	31	Mo	0.794 725	1.298 412
15	O	- 0.404 588	- 0.359 377	32	O	- 0.165 802	- 0.406 912
16	O	- 0.414 800	- 0.744 057	33	O	- 0.176 911	- 0.541 074
17	Mo	0.745 739	1.473 090	34	O	- 0.381 966	- 0.710 451

4 CONCLUSIONS

1) Two possible structures of $Mo_8O_{26}^{4-}$ were optimized using the Polak-Ribiere method of Molecular Mechanics Optimization and the termination condition is RMS (Root-mean-square) gradient of 0.42 kJ/mol. Based on the molecular dynamics, Lengevin dynamics and Monte Carlo dynamics simulation, the models of $Mo_8O_{26}^{4-}$ with the lowest energy were acquired respectively according to the energy of the systems calculated using the ZNDO/1 and PM3 methods. The models of $Mo_8O_{26}^{4-}$ with the lowest energy were determined where the MoO_6 octahedrons and MoO_4 tetrahedrons were contorted to a certain extent.

2) The quantum chemical calculation results show that the contortion of the structure with eight MoO_6 is smaller than that of the structure with six MoO_6 and two MoO_4. The total energies of the two structures are nearly equal because the contortion of the structure with six MoO_6 and two MoO_4 would make the exclusion force decreased.

[REFERENCES]

[1] Shaheen W M, Selim M M. Thermal decompositions of pure and mixed manganese carbonate and ammonium molybdate tetrahydrate [J]. Journal of Thermal Analysis and Calorimetry, 1998, 59(3): 961- 970.

[2] YIN Zhou-lan, CHEN Qi-yuan. Preparation and properties of the microphase and a new phase of ammonium tetramolybdate [J]. Trans Nonferrous Met Soc China, 1997, 7(1): 18- 21.

[3] Khan A J, Abe M, Kanzaki Y. Importance of cubic ammonium molybdate as cation exchanger — Peculiar ion exchange reactions [A]. Proceedings of the International Conference on Ion Exchange ICIE' 91[C]. 1991. 145- 148.

[4] Khulbe K C, Manna R S, Ajaka C D. Characterization of MoO_3-zeolite prepared from ammonium molybdate [J]. Zeolites, 1993, 13(7): 572- 580.

[5] YIN Zhou-lan, LI Xin-hai, ZHAO Qin-sheng. Thermal decomposition of ammonium molybdate mixture [J]. Trans Nonferrous Met Soc China, 1994, 4(3): 46- 49.

[6] Bali K, Geretovszky Z, Toth A L. Quest for high quality local electroless laser deposition from the liquid phase: decomposition of ammonium molybdate [J]. Applied Surface Science, 1985, 69(1): 326- 329 .

[7] Khan A J, Kanzaki Y, Abe M. Nuclear magnetic resonance study of ion-exchange reaction on cubic ammonium molybdate [J]. Journal of the Chemical Society, 1991, 87(16): 2669.

[8] Singh S K. Effect of ammonium molybdate on biomethanation [J]. Renewable Energy, 1995, 6(4): 441- 443.

[9] Watson B A, Barteau M A, Haggerty L. Scanning tunneling microscopy and tunneling spectroscopy of ordered hetero- and isopolyanion arrays on graphite [J]. Langmuir, 1992, 8(4): 1145- 1148.

[10] WU Zheng-ping, YIN Zhou-lan, CHEN Qi-yuan. Study on the effect of ultrasonic on the crystallization of ammonium tetramolybdate [J]. The Chinese Journal of Nonferrous Metals (in Chinese), 2002, 12(1): 196~200.

[11] WANG Er-bo, HU Chang-wen, XU Lin. Polyhydric Chemist Introduction (in Chinese) [M]. Beijing: Chemical Industry Press, 1998. 48- 49.

[12] QIAN Yi-tai. Crystal Chemistry (in Chinese) [M]. Hefei: The University of Science & Technology of China Press, 1988. 258- 261.

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