

氧原子簇 O_x^y ($x=2\sim 6, y=-2\sim 2$) 的结构、能学与光谱性质*

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摘要: 在 B3LYP/6-311G(d,p) 水平上, 对氧原子簇 O_x^y ($x=2\sim 6, y=-2\sim 2$) 的结构、能学与光谱性质进行了量子化学从头计算, 对 3O_2 和 ${}^2O_2^+$ 的基态和激发态进行了 CASSCF 计算。结果表明, 氧分子及其离子的体系总能量大小为 ${}^3O_2({}^3\Sigma_g^-) < {}^2O_2^-({}^2\Pi_g) < {}^1O_2({}^1\Delta_g) < {}^1O_2^{-2}({}^1\Sigma_g^+) < {}^2O_2^+({}^2\Pi_g) < {}^1O_2^{-2}({}^1\Sigma_g^+)$ 。活性的二重态氧分子负离子 ${}^2O_2^-({}^2\Pi_g)$ 在相对能量上只比三重态的中性氧分子 ${}^3O_2({}^3\Sigma_g^-)$ 高 28 kJ/mol。对于弯曲型 (Structure-1) 的臭氧分子 (O_3) 及其离子, 其体系总能量相对次序为 ${}^2O_3^-({}^2B_1) < {}^1O_3({}^1A_1) < {}^3O_3({}^3B_2) < {}^1O_3^{-2}({}^1A_1) < {}^2O_3^-({}^2A_1)$ 。

氧四聚体 (O_4) 及其离子的体系总能量相对大小为 ${}^2O_4^-(C_s \text{ 弯曲型, } {}^2A')$ $< {}^2O_4^-(C_{2v} \text{ 面心三角型, } {}^2A_2)$ $< {}^2O_4^-(D_{2h} \text{ 直线型, } {}^2\Sigma_g^-)$ $< {}^1O_4(C_s \text{ 弯曲型, } {}^1A')$ $< {}^1O_4(D_{2h} \text{ 直线型, } {}^1\Sigma_g^-)$ $< {}^1O_4(D_{4h} \text{ 正方形, } {}^1A_{1g})$ $< {}^1O_4(C_{2v} \text{ 面心三角型, } {}^1A_1)$ $< {}^2O_4^-(D_{4h} \text{ 正方形, } {}^1A_{1g})$ $< {}^2O_4^-(D_{2h} \text{ 直线型, } {}^2\Sigma_g^-)$ $< {}^2O_4^-(C_s \text{ 弯曲型, } {}^1A')$ 。相对能量最低的氧四聚体物种是呈椅形的带一个负电荷的负离子 ${}^2O_4^-(C_s \text{ 弯曲型, } {}^2A')$, 其特征振动频率应出现在 1179 和 1349 cm^{-1} 。共面三角双锥型的 ${}^1O_4(C_{2v}, {}^1A_1)$ 相对能量最低, 其与 A 字型 ($C_{2v}, {}^1A_1$) 可能是共振构型, 特征振动频率位于 1302 cm^{-1} 。氧六聚体 (O_6) 的六边形构型的相对能量较低, 其振动频率的红外强度很弱, 但从其对称性看, 应具有较强的拉曼强度。

以 B3LYP/6-311G(d,p) 方法计算, 并经 0.9614 因子校正的氧分子及其离子的 O-O 振动频率与实验值相当吻合。

关键词: 氧簇; O_2 ; O_3 ; O_4 ; O_5 ; O_6 ; ab initio; 光谱性质; 结构; 能学

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1 引言

随着富勒烯 (C_{60}) 的发现及其化学的发展, 同种轻原子聚集体的研究展示了崭新且奇妙的一页。聚集体可以说是广义的原子簇, 当其所含的原子数不同于该原子通常所构成的分子时, 其各种性质明显不同于个别的分子。最近, 已经有硫簇、碳簇、磷簇和氧簇等的研究结果发表。特别是线性碳链 C_n ($n=2\sim 15$) 的光谱性质和激发态引起了天文化学家和化学物理学家的极大兴趣。我们最近的初步研究结果亦表明, 中性或带电聚集体的形状结构、光谱性质和成键性质及其与表面之间的相互识别和作用等情况与单个分子的情况大不相同。

氧(O)是与人类、环境和工业生产最密切相关的轻元素之一, 是最重要的生命元素, 是大

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气光化学最普遍的探针分子,也是催化氧化反应最有用的氧化剂。在许多表面氧化过程中,活性氧物种(包括中性分子、负离子或正离子)起着关键作用。而氧分子和臭氧分子更是与人类及其生存环境密切相关的。因此,很有必要深入研究氧聚集体的有关性质。Huber 和 Herzberg 的专著收集了 80 年代以前已发表的氧分子(O_2)及其离子的部分实验或理论光谱常数^[1]。90 年代,氧分子(O_2)和臭氧分子(O_3)及其离子的光谱性质在实验或理论上得到了进一步的研究^[2-15]。最近,包含 4~6 个氧原子的中性或离子性氧簇及其激发态的光谱性质与动态学也得到了越来越多的注意^[16,17]。但是,仍有许多问题有待解决,特别是在实验和理论研究中缺乏系统和可比较的数据。有幸的是,量子理论方法和计算机技术的发展使得我们有可能在理论上先行解决这一重要问题。本文将报道我们最近对氧簇(O_{2-6})及其离子的结构、能学和光谱性质进行的较为系统的理论研究结果。

2 计算方法

用 6-311G(d,p)基组和杂化密度泛函 B3LYP 方法进行 O_2 、 O_3 、 O_4 、 O_5 和 O_6 及其离子的几何构型优化和振动频率的 ab initio 计算。计算模型包括直线型、弯曲型以及部分在理论上可能构成的几何构型。用 CASSCF/6-311G(d,p)方法计算三重态 3O_2 和二重态 $^2O_2^+$ 的基态与激发态,取 3 个活性轨道,对 3O_2 和 $^2O_2^+$ 分别取 4 个和 3 个活性电子。对臭氧分子及其离子计算直线型和弯曲型两种构型。对 O_4 ,我们计算了直线型、弯曲型、正方形和面心三角形;对 O_5 ,我们计算了直线型、弯曲型、五边形、A 字型以及共面三角双锥型;对 O_6 ,我们计算了直线型和六边形。B3LYP 方法计算所得的振动频率乘以校正因子 0.9614,以便与实验值更符合。所有计算均使用 GAUSSIAN 94W 程序^[18]。

3 结果与讨论

3.1 O_2 及其离子的能学与振动频率

如表 1 所示,优化的 O-O 键长和计算的振动频率与括号内的实验值相当吻合。氧分子及其离子的体系总能量相对大小为 $^3O_2(^3\Sigma_g^-) < ^2O_2^-(^2\Pi_g) < ^1O_2(^1\Delta_g) < ^1O_2^{-2}(^1\Sigma_g^+) < ^2O_2(^2\Pi_g) < ^1O_2^{+2}(^1\Sigma_g^+)$ 。最稳定的基态氧分子物种是 $^3O_2(^3\Sigma_g^-)$ 。二重态氧分子负离子 $^2O_2^-(^2\Pi_g)$ 在相对能量上只比三重态的中性氧分子 $^3O_2(^3\Sigma_g^-)$ 高 28 kJ/mol,因此,氧分子在固体表面化学吸附后很容易转变成二重态氧分子负离子。而二重态负离子 $^2O_2^-(^2\Pi_g)$ 的 O-O 键长 1.3520 Å 远大于三重态中性 $^3O_2(^3\Sigma_g^-)$ 的 1.2056 Å,所以,前者比后者活性得多。这就是超氧离子 O_2^- 总是在气-固界面的催化氧化反应中起重要作用的原因之一。另一方面,虽然单重态氧 $^1O_2(^1\Delta_g)$ 的 O-O 键长 1.2066 Å 很接近三重态氧 $^3O_2(^3\Sigma_g^-)$ 的 1.2056 Å,但这两个态之间的能量差为 163 kJ/mol,是化学反应的能量级,因此,从三重态氧 3O_2 到单重态氧 1O_2 的转变并不容易。而从前三个态(3O_2 、 $^2O_2^-$ 和 1O_2)到后三个态($^1O_2^{-2}$ 、 $^2O_2^+$ 和 $^1O_2^{+2}$)的转变则更困难得多,因为它们之间的能量差高达 837 kJ/mol 以上。所以,后三个态的氧物种(包括过氧负离子 $^1O_2^{-2}$)在气-固界面催化氧化反应中应该不起重要作用。过氧负离子 $^1O_2^{-2}(^1\Sigma_g^+)$ 的 O-O 键长(1.6249 Å)很大,将其看成是两个单氧负离子的长程结合,或许是更有道理的。此外,值得指出,有关氧正离子 $^1O_2^{+2}$ 的性质是以前尚未报道过的。

表1 O_2 物种及其离子的相对能量、振动频率和键长Table 1 Relative energies, vibrational frequencies and bond lengths of O_2 species and their ions^a

| Species | State | $R_{O-O}/\text{\AA}$ | $\nu_{O-O}^b/\text{cm}^{-1}$ | $E_{\text{rel}}^c/\text{kJ/mol}$ |
|--------------|----------------|-----------------------------------|------------------------------|----------------------------------|
| 3O_2 | $^3\Sigma_g^-$ | 1.2056 (1.20752) | 1577 (1580) | 0 |
| $^2O_2^-$ | $^2\Pi_g$ | 1.3520 (1.35) | 1139 (1090) | 28 |
| 1O_2 | $^1\Delta_g$ | 1.2066 (1.2156) | 1563 (1484) | 163 |
| $^1O_2^{-2}$ | $^1\Sigma_g^+$ | 1.6249 (1.64 - 1.67) ^d | 627 (615 - 545) ^d | 955 |
| $^2O_2^+$ | $^2\Pi_g$ | 1.1066 (1.1164) | 1993 (1905) | 1211 |
| $^1O_2^{+2}$ | $^1\Sigma_g^+$ | 1.0336 | 2368 | 3601 |

a. Calculated at the B3LYP/6-311G (d, p) level. The values in parentheses are reported by Ref [1] except of the noted.

b. Scaled by 0.9614.

c. The zero point energy is -150.3647856 hartrees for the species $^3O_2^-$.

d. The values in parentheses are reported by Ref [2].

我们选4个活性电子和3个活性轨道,用CASSCF/6-311G(d,p)方法计算了 3O_2 的基态($^3\Sigma_g^-$)和激发态($^1\Delta_g$),其O-O键长分别为1.2056和1.2066Å,二者能量差为124 kJ/mol。我们还选了3个活性电子和3个活性轨道,用CASSCF/6-311G(d,p)方法计算了阳离子 $^2O_2^+$ 的基态($^2\Pi_g$)和激发态($^2\Pi_u$),其O-O键长为1.1066Å,二者的能量差为154 kJ/mol。

3.2 O_3 及其离子的化学与振动频率

用B3LYP/6-311G(d,p)方法计算了臭氧的三种可能结构。Structure-I是具有O-O-O钝角的弯曲型构型,Structure-II是具有O-O-O锐角的弯曲型构型,而Structure-III为线型。表2列出这三种构型的 O_3 物种及其离子的相对能量、振动频率和几何构型。

表2 O_3 物种及其离子的相对能量、振动频率和几何构型Table 2 Relative energies, vibrational frequencies and geometries of O_3 species and their ions^a

| Species | Symmetry | State | $R_{O-O}/\text{\AA}$ | $A_{O-O-O}/(^{\circ})$ | $\nu_{O-O}^b/\text{cm}^{-1}$ | $E_{\text{rel}}^c/\text{kJ mol}^{-1}$ |
|--------------|----------|---------|----------------------|------------------------|------------------------------|---------------------------------------|
| Structure-I | | | | | | |
| $^2O_3^-$ | C_{2v} | 2B_1 | 1.3573 | 115.66 | 573 | 0.0 ^e |
| | | | | | 870 | |
| | | | | | 1016 | |
| 1O_3 | C_{2v} | 1A_1 | 1.2579 | 118.17 | 719 | 195 |
| | | | | | 1144 | |
| | | | | | 1201 | |
| 3O_3 | C_{2v} | 3B_2 | 1.2970 | 129.52 | 556 | 281 |
| | | | | | 675 | |
| | | | | | 990 | |
| $^1O_3^{-2}$ | C_{2v} | 1A_1 | 1.5172 | 116.06 | 392 | 724 |
| | | | | | 570 | |
| | | | | | 765 | |

续表 2

| Species | Symmetry | State | $R_{0-0}/\text{\AA}$ | $A_{0-0-0}/(^{\circ})$ | $\nu_{0-0}^b/\text{cm}^{-1}$ | $E_{\text{rel}}/\text{kJ mol}^{-1}$ |
|---------------------|----------------|--------------|----------------------|------------------------|------------------------------|-------------------------------------|
| $^2\text{O}_3^+$ | C_{2v} | 2A_1 | 1.2130 | 134.54 | 652 | 1408 |
| | | | | | 1137 | |
| | | | | | 1145 | |
| Structure - II | | | | | | |
| $^2\text{O}_3^-$ | D_{3h} | $^2A_2'$ | 1.6361 | 60.00 | 806 | 0.0 ^d |
| | | | | | | (308) ^e |
| $^1\text{O}_3$ | D_{3h} | $^1A_1'$ | 1.4294 | 60.00 | 827 | 16 |
| | | | | | 827 | |
| | | | | | 1144 | |
| $^3\text{O}_3$ | D_{3h} | $^3A_1'$ | 1.5594 | 60.00 | 2400 | 262 |
| | | | | | 2653 | |
| $^1\text{O}_3^{-2}$ | D_{3h} | $^1A_1'$ | 1.9444 | 60.00 | 506 | 805 |
| Structure - III | | | | | | |
| $^2\text{O}_3^-$ | $D_{\infty h}$ | $^2\Sigma_g$ | 1.4244 | 180.00 | 651 | 0 ^f |
| | | | | | 714 | (316) ^g |
| $^3\text{O}_3$ | $D_{\infty h}$ | $^3\Sigma_g$ | 1.2955 | 180.00 | 861 | 90 |
| | | | | | 1032 | |
| $^1\text{O}_3$ | $D_{\infty h}$ | $^1\Sigma_g$ | 1.2970 | 180.00 | 207 | 212 |
| | | | | | 859 | |
| | | | | | 1150 | |
| $^1\text{O}_3^{-2}$ | $D_{\infty h}$ | $^1\Sigma_g$ | 1.6492 | 180.00 | 384 | 690 |
| | | | | | 762 | |
| | | | | | 1769 | |
| | | | | | 1769 | |
| $^2\text{O}_3^+$ | $D_{\infty h}$ | $^2\Sigma_g$ | 1.2094 | 180.00 | 318 | 1200 |
| | | | | | 1025 | |
| | | | | | 1335 | |
| $^1\text{O}_3^{-2}$ | $D_{\infty h}$ | $^1\Sigma_g$ | 1.1465 | 180.00 | 430 | 3270 |
| | | | | | 430 | |
| | | | | | 1155 | |
| | | | | | 1746 | |

a. Calculated at the B3LYP/6-311G (d, p) level.

b. Scaled by 0.9614.

c. The zero point energy is -225.5448372 hatrees for the species $^2\text{O}_3^-$ with Structure - I.

d. The zero point energy is -225.4275748 hatrees for the species $^2\text{O}_3^-$ with Structure - II.

e. Compared with d.

f. The zero point energy is -225.4243656 hatrees for the species $^2\text{O}_3^-$ with Structure - III.

g. Compared with d.

由表2可见, Structure-I物种的体系总能量大小为 ${}^2O_3^-(^2B_1) < {}^1O_3(^1A_1) < {}^3O_3(^3B_2) < {}^1O_3^{-2}(^1A_1) < {}^2O_3^+(^2A_1)$ 。在氧三聚体 O_3 的三种结构中, 能量上最稳定的物种是具有 C_{2v} 对称性的 Structure-I 的 ${}^2O_3^-(^2B_1)$, 其 $O-O-O$ 角为 115.66° , $O-O$ 键长为 1.3573 \AA , 体系总能量为 $225.5448372 \text{ hartrees}$, ${}^2O_3^-(C_{2v}, ^2B_1)$ 这一物种是氧三聚体的基态。Structure-II 的 ${}^2O_3^-(D_{3h}, ^2A_1')$ 物种和 Structure-III 的 ${}^2O_3^-(D_{\infty h}, ^2\Sigma_g^-)$ 物种的体系总能量分别比 Structure-I 的 ${}^2O_3^-(C_{2v}, ^2B_1)$ 物种高 308 和 316 kJ/mol 。就物种间的能量差来看, 从负离子物种转变到中性物种或许是可能的, 但, 从负离子转变到正离子则几乎是不可能的。

以 B3LYP/6-311G(d, p) 方法计算, 并经 0.9614 因子校正的大部分 O_3 及其离子的 $O-O$ 振动频率都是以前尚未报道的, 还有待今后实验验证。

3.3 O_4 及其离子的能学与振动频率

表3列出所计算的氧四聚体(O_4)物种优化的 $O-O$ 键长、键角和计算的振动频率及其归属。从相对能量看, 氧四聚体体系总能量的大小为 ${}^2O_4^-(C_s \text{ 弯曲型}, ^2A')$ $< {}^2O_4^-(C_{2v} \text{ 面心三角型}, ^2A_2) < {}^2O_4^-(D_{\infty h} \text{ 直线型}, ^2\Sigma_g^-) < {}^1O_4(C_s \text{ 弯曲型}, ^1A')$ $< {}^1O_4(D_{\infty h} \text{ 直线型}, ^1\Sigma_g^-) < {}^1O_4(D_{4h} \text{ 正方形}, ^1A_{1g}) < {}^1O_4(C_{2v} \text{ 面心三角型}, ^1A_1) < {}^2O_4^-(D_{4h} \text{ 正方形}, ^1A_{1g}) < {}^2O_4^+(D_{\infty h} \text{ 直线型}, ^2\Sigma_g^+) < {}^2O_4^+(C_s \text{ 弯曲型}, ^1A')$ 。相对能量最低的氧四聚体物种是呈椅形的带一个负电荷的负离子 ${}^2O_4^-(C_s \text{ 弯曲型}, ^2A')$, 这时, $O1-O2$ 键长为 1.2645 \AA , $O3-O4$ 键长为 1.2810 \AA , 较之氧分子的 $O-O$ 键长 1.20752 \AA , 已大大拉长活化, 而 $O2-O3$ 的间距达到 2.9679 \AA , 说明这两对氧二聚体(O_2)之间可能是以较弱的“氧键”联系在一起。理论计算表明, 从两个氧分子($O_2 + O_2$)到氧四聚体(${}^2O_4^-$)的能量得益为 21912 kJ/mol 。比较相对能量较低的前三个氧四聚体负离子(O_4^-)物种, 从弯曲型变到面心三角型和直线型的能量间隔分别为 15928 和 54124 kJ/mol , 而到中性四聚体和四聚体正离子的能量间隔则更高得多。因此, 可以说, 从能量有利方面看来, 氧四聚体应以弯曲型的负离子(O_4^-)形式存在, 其特征振动频率应出现在 1179 和 1349 cm^{-1} , 有别于氧分子(O_2)及氧三聚体(O_3)的特征振动频率。已报道氧分子基态 ${}^3O_2(^3\Sigma_g^-)$ 的特征振动频率为 1580 cm^{-1} (实验值) 或 1577 cm^{-1} (计算值), $O_2^-(^2\Pi_g)$ 的特征振动频率为 1090 cm^{-1} (实验值) 或 1139 cm^{-1} (计算值), 氧三聚体基态 ${}^2O_3^-(^2B_1)$ 的特征振动频率为 870 cm^{-1} (计算值)。

3.4 O_5 及其离子的能学与振动频率

用 B3LYP/6-311G(d, p) 方法计算了四种几何构型的氧五聚体(O_5)物种及其离子的相对能量和振动频率。从表4可见, 共面三角双锥型的相对能量最低, 但 A 字型的相对能量仅较共面三角双锥型的相对能量高 0.08 kJ/mol , 二者的振动频率亦几乎一样, 因此, 可以说这两种构型是共振构型。五边型构型的相对能量较前二者高 1163 kJ/mol , 而直线型的相对能量则高达 77065 kJ/mol , 因此, 氧五聚体要以直线型存在是相当困难的。共面三角双锥型的特征振动频率位于 1302 cm^{-1} 。

3.5 O_6 及其离子的能学与振动频率

对氧六聚体(O_6), 我们研究了六边型和直线型两种构型。如表5所示, 六边型的相对能量较低, 直线型的则较高 156841 kJ/mol 。它们振动频率的红外强度很弱, 难以观测到, 但从其对称性看, 应具有较强的拉曼强度, 应可用拉曼光谱来观测。注意到 O_5 和 O_6 出现多个虚频, 说明它们可能极不稳定, 是亚稳态, 另外也可能是计算的方法和基组选取不够妥当(对于原子数大于5的氧簇), 这有待今后进一步的工作。

表 3 O_4 物种及其离子的相对能量、振动频率和几何构型
 Table 3 Relative energies, vibronic frequencies and geometries of O_4 species and their ions ^a

| Species | Sym. | State | $R_{O-O}/\text{\AA}$ | $A_{O-O-O}/(^{\circ})$ | $\nu_{O-O}^b/\text{cm}^{-1}$ | $E_{rel}/\text{kJ mol}^{-1}$ |
|----------------------------------|----------------|--------------|-----------------------|------------------------|--|------------------------------|
| $^2O_4^-$ bent | C_4 | $^2A'$ | R1 = 1.2645 | A1 = 121.782 | 33(0A''), 38(0A'), | 0.0 |
| | | | R2 = 2.9679 | A2 = 121.525 | 68(0A'), 154(0A') | |
| | | | R3 = 1.2810 | A3 = 180 | 1179(1982A'), 1349(57A') | |
| $^2O_4^-$ face-centered triangle | C_{2v} | 2A_2 | R1 = 1.2382 | A1 = 76.479 | 91(0B ₁), 100(4A ₁), | 15928 |
| | | | R2 = 2.6479 | A2 = 166.479 | 228(0B ₂), | |
| | | | R3 = 1.3065 | A3 = 180 | 1145(1027A ₁), 1395(367A ₁), (1) | |
| $^2O_4^-$ linear | $D_{\infty h}$ | $^2\Sigma_g$ | R1 = R3 = 1.2751 | A1 = A2 = 180 | 251(0Σ _g), 318(0Π _g), | 54124 |
| | | | R2 = 2.0865 | A3 = 0 | 423(0Π _g), 1209(986Σ _u), 1329(0Σ _g), (2) | |
| | | | | | | |
| 1O_4 bent | C_4 | $^1A'$ | R1 = 1.2045 | A1 = 89.998 | 225(18A'), 500(0A'), | 85542 |
| | | | R2 = 1.9497 | A2 = 180 | 517(0A''), 766(0A'), | |
| | | | R3 = 1.2044 | A3 = 89.991 | 1376(509A'), 1552(0A') | |
| 1O_4 linear | $D_{\infty h}$ | $^1\Sigma_g$ | R1 = 1.2027 | A1 = 180 | 351(0Σ _g), 510(0Π _g) | 139620 |
| | | | R2 = 1.9237 | A2 = 180 | 510(0Π _g), 1446(886Σ _u) | |
| | | | R3 = 1.2027 | A3 = 0 | 1581(0Σ _g), (2) | |
| 1O_4 square | D_{4h} | $^1A_{1g}$ | R1 = R2 = 1.4695 | A1 = A2 = 90 | 775(0B _{1g}), 841(4E _u) | 188159 |
| | | | R3 = 1.4695 | A3 = 0 | 841(4E _u), 901(0A _{1g}) | |
| | | | | | 1007(0B _{2g}), (1) | |
| 1O_4 face-centered triangle | C_{2v} | 1A_1 | R1 = 1.5151 | A1 = 58.674 | 216(0B ₂), 519(33B ₂) | 297913 |
| | | | R2 = 1.4571 | A2 = 148.674 | 525(2A ₁), 870(27A ₁), | |
| | | | R3 = 1.3868 | A3 = 180 | 878(12A ₁), (1) | |
| $^2O_4^-$ square | D_{4h} | $^1A_{1g}$ | R1 = R2 = R3 = 3.3593 | A1 = A2 = 90 A3 = 0 | 04bmfreq. out | 356736 |
| $^2O_4^+$ linear | $D_{\infty h}$ | $^1\Sigma_g$ | R1 = 1.1503 | A1 = A2 = 180 | 235(0Σ _g), 283(0Π _g), | 467093 |
| | | | R2 = 2.1287 | A3 = 0 | 413(0Π _g), | |
| | | | R3 = 1.1503 | | 1659(852Σ _u), 1787(0Σ _g), (2) | |

a. Calculated at the B3LYP/6-311G (d, p) level.

b. The frequencies were scaled by 0.9614, following with IR intensity and symmetry in parentheses. The value in the last parentheses is the number of imaging frequencies.

c. The zero point energy is -300.7534335hartrees for the species $^2O_4^-$ with geometry of bent-type.

表 4 O_5 物种及其离子的相对能量、振动频率和几何构型Table 4 Relative energies, vibronic frequencies and geometries of O_5 species and their ions^a

| Species | Sym. | State | $R_{0-0}/\text{\AA}$ | $A_{0-0-0}/(^{\circ})$ | $\nu_{0-0}^b/\text{cm}^{-1}$ | $E_{\text{rel}}/\text{kJ mol}^{-1}$ |
|---|-----------------|----------------|----------------------|------------------------|------------------------------------|-------------------------------------|
| 1O_5 coplanar - triangle - bicone | C_{2v} | 1A_1 | R1 = R2 | A1 = 143.613 | 149($0A_1$), 239($0A_2$), | 0.0 ^c |
| | | | = 2.3615 | A2 = A3 = 18.193 | 338($1A_1$), 484($7B_2$), | |
| | | | R3 = 4.4869 | A4 = A10 = 114.93 | 808($23A_1$), | |
| | | | R4 = R6 | A5 = A9 = 28.683 | 1302($951B_2$), | |
| | | | = 1.6278 | A6 = A12 = 39.93 | 1408($25A_1$), (2) | |
| | | | R5 = R7 | A7 = A13 = 21.737 | | |
| | | | = 1.2173 | A8 = A14 | | |
| | | | | = 111.387 | | |
| | | | | A11 = 86.247 | | |
| | | | | D1 ~ D8 = 360 | | |
| | D9, 10, 12, 13, | | | | | |
| | 15, 16 = 180 | | | | | |
| | D11, 14, 17 = 0 | | | | | |
| 1O_5 A - type | C_{2v} | 1A_1 | R1 = 1.6281 | A1 = 46.859 | 149($0A_1$), 238($0A_2$), | 0.08 |
| | | | R2 = 2.2265 | A2 = A4 = 158.215 | 338($1A_1$), 484($7B_2$), | |
| | | | R3 = R4 | A3 = A5 = 0 | 808($23A_1$), | |
| | | | = 1.2172 | | 1302($951B_2$), | |
| | | | 1408($25A_1$), (2) | | | |
| 1O_5 pentagon | D_{5h} | ${}^1A_1'$ | R1 = R2 = | A1 = A2 = | 685($0E_2'$), 685($0E_2'$), | 1163 |
| | | | R3 = R4 | A4 = 108 | 793($0A_1'$), 870($2E_1'$), | |
| | | | = 1.4473 | A3 = A5 = 0 | 870($2E_1'$), 883($0E_2'$), | |
| | | | | | 883($0E_2'$), (2) | |
| 1O_5 linear | $C_{\infty v}$ | ${}^1\Sigma_g$ | R1 = 1.2056 | A1 = A2 | 293(0Σ), 366(0Π), | 77065 |
| | | | R2 = 1.8938 | = A4 = A5 = 180 | 366(0Π), 816(226Σ), | |
| | | | R3 = 1.2878 | A3 = 0 | 1121(16Σ), | |
| | | | R4 = 1.3150 | | 1491(616Σ), (4) | |

a. Calculated at the B3LYP/6-311G (d, p) level.

b. The frequencies were scaled by 0.9614, following with IR intensity and symmetry in parentheses. The value in the last parentheses is the number of imaging frequencies.

c. The zero point energy is -375.7214354 hartrees for the species 1O_5 with geometry of coplanar triangular cone.

表 5 O_6 物种及其离子的相对能量、振动频率和几何构型Table 5 Relative energies, vibronic frequencies and geometries of O_6 species and their ions^a

| Species | Sym. | State | $R_{O-O}/\text{\AA}$ | $A_{O-O-O}/(^{\circ})$ | $\nu_{O-O}^b/\text{cm}^{-1}$ | $E_{\text{rel}}/\text{kJ mol}^{-1}$ |
|-------------------|----------------|----------------|----------------------|------------------------|--|-------------------------------------|
| 1O_6 hexagon | D_{2h} | 1A_g | R1 = 3.2741 | A1 = A2 = 90 | 31($0B_{2u}$), 42($0A_g$), | 0.0 ^c |
| | | | R2 = 1.4305 | A3 = 0 | 822($9B_{1u}$), 827($0B_{3g}$), | |
| | | | R3 = 3.2741 | A4 = A6 = 59.967 | 828($7B_{2u}$), 828($0A_g$), | |
| | | | R4 = 1.4290 | | 1143(B_{1u}), 1143(A_g), | |
| | | | R5 = 1.4290 | A5 = A7 = 180 | (4) | |
| 1O_6 linear | $D_{\infty h}$ | ${}^1\Sigma_g$ | R1 = R5 | A1 = A2 = A3 | 234($0\Sigma_g$), 244($0\Pi_g$), | 156841 |
| | | | = 1.3178 | = A4 = A6 = 180 | 244($0\Pi_g$), | |
| | | | R2 = R4 | A5 = A7 = 0 | 775($560\Sigma_u$), | |
| | | | = 1.2808 | | 847($0\Sigma_g$), 1164($0\Sigma_u$), | |
| | | | R3 = 1.9169 | | 1204($0\Sigma_g$), (6) | |

a. Calculated at the B3LYP/6-311G (d, p) level.

b. The frequencies were scaled by 0.9614, following with IR intensity and symmetry in parentheses. The value in the last parentheses is the number of imaging frequencies.

c. The zero point energy is -450.8427313hartrees for the species 1O_6 with geometry of hexagon-type.

4 结 论

我们对氧簇(O_2 、 O_3 、 O_4 、 O_5 和 O_6 及其离子)的几何构型、能与振动频率进行了量子化学从头计算。对 O_2 及其离子的B3LYP/6-311G(d, p)计算表明,在体系总能量上的大小为 ${}^3O_2({}^3\Sigma_g^-) < {}^2O_2^{-}({}^2\Pi_g) < {}^1O_2({}^1\Delta_g) < {}^1O_2^{-}({}^1\Sigma_g^+) < {}^2O_2^{-}({}^2\Pi_g) < {}^1O_2^{-}({}^1\Sigma_g^+)$ 。对 O_3 及其离子的B3LYP/6-311G(d, p)计算表明,在体系总能量上的大小为 ${}^2O_3^{-}({}^2B_1) < {}^1O_3({}^1A_1) < {}^3O_3({}^3B_2) < {}^1O_3^{-}({}^1A_1) < {}^2O_3^{+}({}^2A_1)$ 。 O_2 及其离子的基态是 ${}^3O_2({}^3\Sigma_g^-)$,其O-O键长为1.2056 Å, O-O键振动频率为1577 cm^{-1} 。 O_3 及其离子的基态是 ${}^2O_3^{-}({}^2B_1)$,其O-O键长为1.3573 Å, O-O-O键角为115.6584°。二重态 ${}^2O_2^{-}({}^2\Pi_g)$ 与三重态 ${}^3O_2({}^3\Sigma_g^-)$ 之间的能隙仅28 kJ/mol,很容易通过氧分子在固体表面的化学吸附而转变,但二重态负离子 ${}^2O_2^{-}({}^2\Pi_g)$ 却比三重态中性的 ${}^3O_2({}^3\Sigma_g^-)$ 活性得多,前者的O-O键长为1.3520 Å,远大于后者的1.2056 Å,对 O_3 及其离子的三种几何构型计算表明, O-O-O为钝角的弯曲型构型I(即Structure-I)在体系总能量上较之O-O-O为锐角的弯曲型构型II(即Structure-II)和直线型(即Structure-III)都来得有利。

对 O_4 及其离子的B3LYP/6-311G(d, p)计算表明,在体系总能量上的大小为 ${}^2O_4^{-}(C_s \text{ 弯曲型}, {}^2A') < {}^2O_4^{-}(C_{2v} \text{ 面心三角型}, {}^2A_2) < {}^2O_4^{-}(D_{\infty h} \text{ 直线型}, {}^2\Sigma_g^-) < {}^1O_4(C_s \text{ 弯曲型}, {}^1A') < {}^1O_4(D_{\infty h} \text{ 直线型}, {}^1\Sigma_g^-) < {}^1O_4(D_{4h} \text{ 正方形}, {}^1A_{1g}) < {}^1O_4(C_{2v} \text{ 面心三角型}, {}^1A_1) < {}^2O_4^{-}(D_{4h} \text{ 正方形}, {}^1A_{1g}) < {}^2O_4^{-}(D_{\infty h} \text{ 直线型}, {}^2\Sigma_g^-) < {}^2O_4^{+}(C_s \text{ 弯曲型}, {}^1A')$ 。相对能量最低的氧四聚体物种是呈椅形的带一个负电荷的负离子 ${}^2O_4^{-}(C_s \text{ 弯曲型}, {}^2A')$,其特征振动频率应出现在1179和1349 cm^{-1} 。对 O_5 及其离子的B3LYP/6-311G(d, p)计算表明,共面三角双锥型的相对能量最低,其与A字型可能是共振构型,特征振动频率位于1302 cm^{-1} 。氧六聚体(O_6)的六边形相对能量较低,其振动频率的红外强度很弱,但从其对称性看,应具有较强的拉曼强度。

以 B3LYP/6-311G (d,p) 方法计算, 并经 0.9614 因子校正的 O-O 振动频率与已报道的实验值非常吻合。而 ${}^1O_2^{-2}({}^1\Sigma_g^+)$ 物种的 O-O 振动频率 2368 cm^{-1} 以及大部分 O_3 、 O_4 、 O_5 和 O_6 及其离子的振动频率都是以前尚未报道的。

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Geometries, Energetics and Spectroscopic Properties of Oxygen Clusters O_x^y ($x=2\sim 6, y=-2\sim 2$)^{*}

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Abstract The geometries, energetics and spectroscopic properties of oxygen clusters, O_x^y ($x=2\sim 6, y=-2\sim 2$), were investigated at the B3LYP/6-311G (d,p) level. The CASSCF calculations were carried out for the ground and excited states of 3O_2 and ${}^2O_2^+$. The total energy is ${}^3O_2({}^3\Sigma_g^-) < {}^2O_2^-({}^2\Pi_{gi}) < {}^1O_2({}^1\Delta_g) < {}^1O_2^{-2}({}^1\Sigma_g^+) < {}^2O_2^+({}^2\Pi_g) < {}^1O_2^{+2}({}^1\Sigma_g^+)$. The relative energy of the active doublet anion of oxygen molecule, ${}^2O_2^-({}^2\Pi_{gi})$, is only 28 kJ/mol higher than the triplet neutral oxygen molecule, ${}^3O_2({}^3\Sigma_g^-)$. The calculated O-O vibrational frequencies all are in good

agreement with the experimental values. They are 1577 (1580), 1139 (1090), 1563 (1484), 627 (615 ~ 545) and 1993 (1905) cm^{-1} , where the O - O vibrational frequency values in parentheses are experimental values, for ${}^3\text{O}_2$ (${}^3\Sigma_g^-$), ${}^2\text{O}_2^-$ (${}^2\Pi_{g1}$), ${}^1\text{O}_2$ (${}^1\Delta_g$), ${}^1\text{O}_2^{-2}$ (${}^1\Sigma_g^+$) and ${}^2\text{O}_2^+$ (${}^2\Pi_g$), respectively. Moreover, the O - O vibrational frequency of ${}^1\text{O}_2^{+2}$ (${}^1\Sigma_g^+$) was computed as 2368 cm^{-1} which has not been reported before at both experimental and theoretical levels.

Both bent and linear geometries of O_3 were studied. The bent - types of O_3 are more favorable than the linear - type in energy. Three types of structure for oxygen trimers are calculated at the B3LYP/6 - 311G (d, p) level. They are the structure - I with an obtuse angle of O - O - O, the structure - II with an acute angle of O - O - O, and the structure - III of linear type. For a bent - type structure of O_3 species (structure - I), the total energy is ${}^2\text{O}_3^-$ (${}^2\text{B}_1$) < ${}^1\text{O}_3$ (${}^1\text{A}_1$) < ${}^3\text{O}_3$ (${}^3\text{B}_2$) < ${}^1\text{O}_3^{-2}$ (${}^1\text{A}_1$) < ${}^2\text{O}_3^+$ (${}^2\text{A}_1$). The optimization of geometry at B3LYP/6 - 311G (d, p) level indicated that the species of ${}^2\text{O}_3^-$ (${}^2\text{B}_1$) with 1.3573 Å of O - O bond length and 115.6584° of O - O - O bond angle is the ground state of O_3 .

The total energy of O_4 species and their ions is ${}^2\text{O}_4^-$ (C_s , ${}^2\text{A}'$, bend - type) < ${}^2\text{O}_4^-$ (C_{2v} , ${}^2\text{A}_2$, face - centered triangle - type) < ${}^2\text{O}_4^-$ ($\text{D}_{\infty h}$, ${}^2\Sigma_g$, linear - type) < ${}^1\text{O}_4$ (C_s , ${}^1\text{A}'$, bend - type) < ${}^1\text{O}_4$ ($\text{D}_{\infty h}$, ${}^1\Sigma_g$, linear - type) < ${}^1\text{O}_4$ (D_{4h} , ${}^1\text{A}_{1g}$, square - type) < ${}^1\text{O}_4$ (C_{2v} , ${}^1\text{A}_1$, face - centered triangle - type) < ${}^2\text{O}_4^-$ (D_{4h} , ${}^1\text{A}_{1g}$, square - type) < ${}^2\text{O}_4^+$ ($\text{D}_{\infty h}$, ${}^2\Sigma_g$, linear - type) < ${}^2\text{O}_4^+$ (C_s , ${}^1\text{A}'$, bend - type). The species with the lowest relative energy is an anion, ${}^2\text{O}_4^-$ (C_s , ${}^2\text{A}'$, bend - type), with chair form geometry and characteristic vibronic frequencies of 1179 and 1349 cm^{-1} . The relative energy of ${}^1\text{O}_5$ (C_{2v} , ${}^1\text{A}_1$) with coplanar - triangle - bicone geometry is the lowest among the O_5 species and their ions, which may be a resonance structure with ${}^1\text{O}_5$ (C_{2v} , ${}^1\text{A}_1$) of A - type. Their characteristic vibronic frequency is 1302 cm^{-1} . The relative energy of the O_6 species and their ions with hexagon geometry is lower than one with linear geometry. Their infrared vibronic intensity may be weak and unobservable but the Raman vibronic intensity may be strong and observable based on their symmetry.

Key words Oxygen cluster, O_2 , O_3 , O_4 , O_5 , O_6 , ab initio, Spectroscopic properties, Geometry, Energetics

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