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Matrix isolation infrared spectroscopic and density functional theoretical study of the aluminum, gallium and indium borates

Guangjun Wang, Mohua Chen, Gongyu Jiang, Han Zhou, Mingfei Zhou *

Department of Chemistry, Laser Chemistry Institute, Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials, Fudan University, No. 220, Handan Road, Shanghai 200433, PR China

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Abstract

The aluminum, gallium and indium borates have been produced by co-deposition of metal and boron atoms with oxygen molecules in excess argon at low temperature. The metal borate molecules were identified on the basis of the experimentally observed vibrations with isotopic effects ($^{16}O/^{18}O$ substitutions, and $^{10}B/^{11}B$ and $^{69}Ga/^{71}Ga$ in natural abundance) as well as density functional calculations. The aluminum, gallium and indium borates were predicted to have linear geometries with a highly ionic electronic structure.

1. Introduction

The oxides of group 13 (boron, aluminum, gallium and indium) possess versatile structures and functions, and are widely used in catalytic and optical material fields. Recent investigations have shown that heteroatom incorporation or doping can improve the properties of group 13 metal oxide materials [1–5]. For example, Al_2O_3 is a widely used catalyst and catalyst supporter for petroleum refining, coal liquefaction and organic synthesis. It is found that incorporation of boron into Al_2O_3 can improve the activity or selectivity of the catalyst [1–3]. As a kind of glass, some borates of alkali, alkaline earth or rare earth metals are of interest from a view point of nonlinear optical property. It is reported that some properties of the borates were significantly improved when part of B was substituted by Al, Ga or In [4,5].

The reactions of group 13 metal atoms with oxygen and the geometrical, electronic and bonding properties of small metal oxide clusters provide useful information in understanding the structure and bonding between group 13 metal and oxygen, and have been extensively studied both experimentally and theoretically [6–18]. It was found that the boron atoms reacted with oxygen to form the linear OBO insertion molecule in solid argon [6], while the Al, Ga and In atoms reacted with O_2 to form the cyclic $M(O_2)$, which rearranged to the more stable linear OMO isomer upon excitation [7]. The previous studies were focused on the binary metal oxide species, and the ternary oxides of group 13 metals have not been reported. In this paper we present a matrix isolation infrared spectroscopic and density functional theory study of the MOBO (M = Al, Ga, and In) molecules.

2. Experimental and computational methods

The experimental setup for pulsed laser ablation and matrix isolation infrared spectroscopic investigation has

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* Corresponding author. Tel.: +86 2165643532; fax: +86 2165643532.
E-mail address: mfzhou@fudan.edu.cn (M. Zhou).

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been described previously [19]. Briefly, the 1064 nm Nd:YAG laser fundamental (Spectra Physics, DCR 150, 20 Hz repetition rate and 8 ns pulse width) was focused onto the rotating metal targets through a hole in a CsI window, which was mounted on a cold tip of a closed-cycle helium refrigerator (Air Products, Model CSW202). Typically, 5–10 mJ/pulse laser energy was used. The ablated boron and metal atoms were co-deposited with molecular oxygen in excess argon onto the 12 K CsI window for one to two hours at a rate of approximately 5 mmol/h. The mixed metal targets were prepared by pressing the mixtures of boron and metal powders. Natural abundance boron powders (^{10}B: 19.8%, ^{11}B: 80.2%, Merck), aluminum, gallium (^{69}Ga: 60%, ^{71}Ga: 40%) and indium particles (Shanghai Chemical Reagent Corporation, >99.99%) were used in the experiments. $^{16}O_2$ and $^{18}O_2$ (99%, Isotec) were used to prepare the O_2/Ar mixtures. After sample deposition, infrared spectra were recorded on a Bruker IFS113v spectrometer at 0.5 cm^{-1} resolution with a DTGS detector in the spectral range of 4000–400 cm^{-1}. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband irradiation using a 250-W high-pressure mercury arc lamp.

Density functional theory calculations (DFT) were performed using the Gaussian 03 program [20]. The most popular Becke's three-parameter hybrid functional, with additional correlation corrections due to Lee, Yang, and Parr was utilized (B3LYP) [21,22]. The 6-311+G* basis set for B, O, Al, and Ga, and Lanl2dz pseudopotential and basis for In were used [23–25]. Geometries were fully optimized and vibrational frequencies calculated with analytical second derivatives, and zero point vibrational energies were derived.

3. Result and discussion

The reactions of laser-ablated boron, aluminum, gallium and indium atoms with oxygen in solid argon have been investigated previously [6,7]. We first repeated these experiments, and the resulting infrared spectra are about the same as those reported previously. When the mixed B/Al, B/Ga or B/In targets were used, new product absorptions were produced. The band positions are listed in Table 1. Representative infrared spectra in the 2080–1960 cm^{-1} region from co-deposition of laser-ablated B/Ga atom mixtures (using a B:Ga molar ratio = 2:1 target) with 0.2% O_2 in argon are shown in Fig. 1. The experiments were repeated with the $^{18}O_2$, $^{18}O_2 + {}^{16}O_2$ and $^{18}O_2 + {}^{18}O^{16}O + {}^{16}O_2$ samples, and the isotopic counterparts of the new product absorptions are also listed in Table 1. The spectra in selected regions with different isotopic O_2 samples after 30 K annealing are shown in Figs. 2–4, respectively.

Reactions of B/Al, B/Ga, and B/In atoms with oxygen molecules revealed new absorptions in the 2100–1900 cm^{-1} region (Table 1). Taking the B/Ga system as an example, two weak doublet absorptions at 2063.4/2061.8 and 1993.6/1992.3 cm^{-1} were observed on sample deposition when a target mixed with natural abundance boron and gallium was used (Fig. 1). These absorptions increased together on 25 and 33 K annealing, and kept almost unchanged upon broadband irradiation. The 2063.4/2061.8 cm^{-1} doublet is approximately 25% in intensity of the 1993.6/1992.3 cm^{-1} doublet, which clearly indicates that only one boron atom is involved in the vibrational mode. The relative intensities of the 1993.6 and 1992.3 cm^{-1} bands matched natural isotopic abundance gallium (^{69}Ga: 60%, ^{71}Ga: 40%) [26] and confirms that only one gallium atom is involved in the mode. These absorptions shifted to 2038.4/2037.1 and 1963.5/1962.1 cm^{-1} with $^{18}O_2$ (Fig. 3, trace c). The isotopic frequency ratios (^{10}B/^{11}B (^{69}Ga): 1.0350, ^{16}O/^{18}O (^{11}B^{69}Ga): 1.0153) imply that these absorptions are mainly due to terminal B–O stretching vibrations. In the spectrum when a scrambled $^{18}O_2 + {}^{18}O^{16}O + {}^{16}O_2$ sample was used (Fig. 3, trace b), each band split into a quartet with approximately 1:1:1:1: relative intensities, indicating that two inequivalent O atoms are involved in the vibration. These observations demonstrated that the new product molecule has the $BGaO_2$ stoichiometry with two inequivalent O atoms. Accordingly, we assign the 2063.4/2061.8 and 1993.6/1992.3 cm^{-1} absorptions to the B–O stretching vibrations of the GaOBO isotopomers.

Similar absorptions at 2086.5 and 2016.1 cm^{-1} in the B/Al + O_2 experiments (B:Al molar ratio: 1:2), and

Table 1
Infrared absorptions (cm^{-1}) of the MOBO (M = Al, Ga and In) molecules in solid argon

$^{16}O_2$	$^{18}O_2$	$^{16}O_2 + {}^{18}O_2$	$^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$	Assignment
2086.5	2057.5	2086.5, 2057.5	2086.5, 2079.8, 2064.3, 2057.5	AlO^{10}BO
2016.1	1985.5	2016.1, 1985.5	2016.1, 2009.1, 1993.2, 1985.5	AlO^{11}BO
2063.4	2038.4	2063.4, 2038.4	2063.4, 2051.6, 2042.2, 2038.4	^{69}GaO^{10}BO
2061.8	2037.1	2061.8, 2037.1	2061.8, 2049.5, 2040.5, 2037.1	^{71}GaO^{10}BO
1993.6	1963.5	1993.6, 1963.5	1993.6, 1986.6, 1971.7, 1963.5	^{69}GaO^{11}BO
1992.3	1962.1	1992.3, 1962.1	1992.3, 1985.2, 1970.1, 1962.1	^{71}GaO^{11}BO
2049.4	2015.2	2049.4, 2015.2	2049.4, 2039.8, 2029.3, 2015.2	InO^{10}BO
1979.9	1950.4	1979.9, 1950.4	1979.9, 1972.1, 1959.0, 1950.4	InO^{11}BO

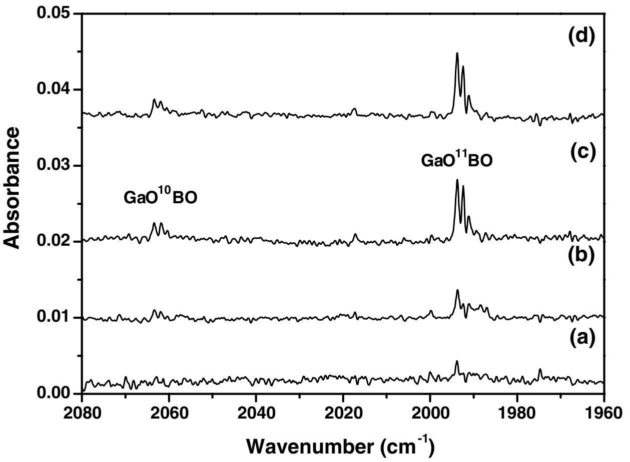

Fig. 1. Infrared spectra in the 2080–1960 cm^{-1} region from co-deposition of laser-ablated B and Ga atoms with 0.2% O_2 in argon. (a) 1 h of sample deposition at 12 K, (b) after 25 K annealing, (c) after 33 K annealing, and (d) after 20 min of broad band irradiation.

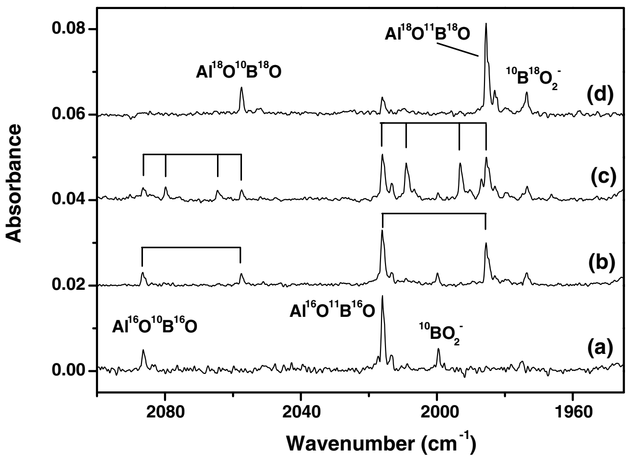

Fig. 2. Infrared spectra in the 2100–1940 cm^{-1} region from co-deposition of laser-ablated B and Al atoms with isotopic O_2 samples in argon. Spectra were taken after 2 h of sample deposition followed by 30 K annealing. (a) 0.2% $^{16}O_2$, (b) 0.2% $^{16}O_2$ + 0.2% $^{18}O_2$, (c) 0.125% $^{16}O_2$ + 0.25% $^{16}O^{18}O$ + 0.125% $^{18}O_2$, and (d) 0.2% $^{18}O_2$.

2049.4 and 1979.9 cm^{-1} in the B/In + O_2 experiments (B:In molar ratio:1:1) are assigned to the AlO^{10}BO/AlO^{11}BO and InO^{10}BO/InO^{11}BO molecules, respectively, following the example of GaOBO.

Density functional theory calculations support the experimental assignment and provide insight into the electronic structure and bonding in MOBO (M = Al, Ga and In). The B3LYP calculations predicted the MOBO molecules to have linear structures. The geometrical parameters and some electronic properties for the computed equilibrium structure are presented in Table 2. The calculations indicated that the linear MOBO structure is the global minimum on the potential energy surfaces of BMO_2. We also computed all the other possible structural isomers with BMO_2 formula, such as OBMO, BOMO, BMO_2, MBO_2, and cyclic-B(μ-O_2)M. All of these isomers are higher in energy than MOBO by more than 60 kcal/mol.

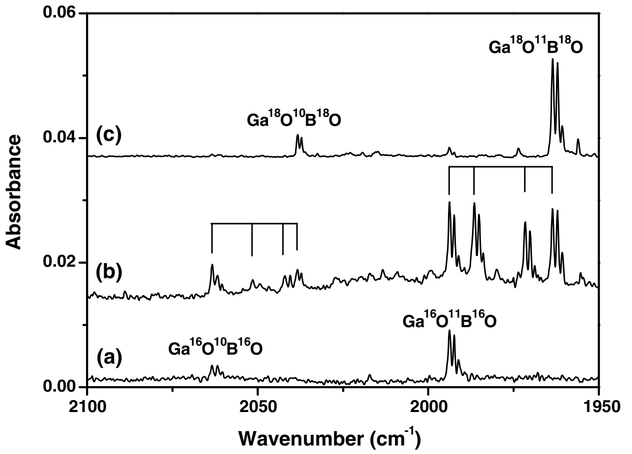

Fig. 3. Infrared spectra in the 2100–1950 cm^{-1} region from co-deposition of laser-ablated B and Ga atoms with isotopic substituted O_2 samples in argon. Spectra were taken after sample deposition followed by 30 K annealing. (a) 0.2% $^{16}O_2$, (b) 0.125% $^{16}O_2$ + 0.25% $^{16}O^{18}O$ + 0.125% $^{18}O_2$, and (c) 0.2% $^{18}O_2$.

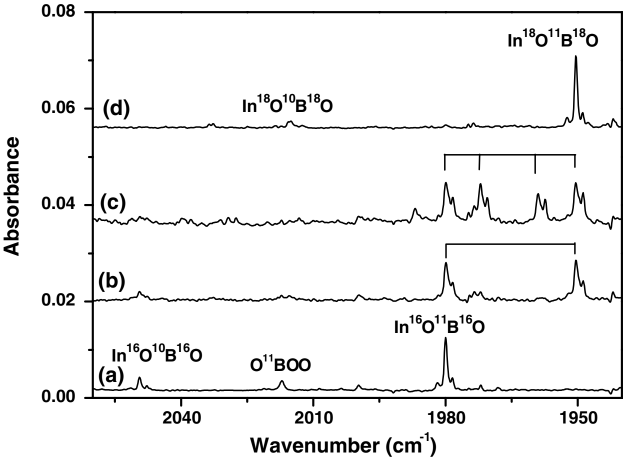

Fig. 4. Infrared spectra in the 2060–1940 cm^{-1} region from co-deposition of laser-ablated B and In atoms with isotopic substituted O_2 samples in argon. Spectra were taken after 2 h of sample deposition followed by 30 K annealing. (a) 0.2% $^{16}O_2$, (b) 0.2% $^{16}O_2$ + 0.2% $^{18}O_2$, (c) 0.15% $^{16}O_2$ + 0.3% $^{16}O^{18}O$ + 0.15% $^{18}O_2$, and (d) 0.2% $^{18}O_2$.

Table 2
Calculated geometrical (bond length in Å) and electronic properties of MOBO (M = Al, Ga and In)

	AlOBO	GaOBO	InOBO
$R_{M–O}$	1.763	1.880	2.013
$R_{O–B}$	1.307	1.303	1.299
$R_{B–O}$	1.218	1.221	1.224
E (a.u.)[a]	−417.942799	−2100.357107	−177.381222
q_M	+0.884	+0.875	+0.918

[a] After zero point energy corrections.

Table 3
Calculated vibrational frequencies (cm^{-1}) and intensities (km/mol) of the $MO^{11}BO$ molecules (M = Al, Ga and In)

	Frequency (intensity, mode)
OBO ($^2\Pi_g$)	422.2 (83, π_u) 509.7 (65, π_u) 1089.0 (0, σ_g) 1472.2 (474, σ_u)
OBO^- ($^1\Sigma_g^+$)	597.1 (47, π_u) 597.1 (47, π_u) 1095.2 (0, σ_g) 1954.8 (740, σ_u)
AlOBO ($^1\Sigma$)	80.7(0, π) 80.7(0, π) 512.0 (104, σ) 539.0 (61, π) 539.0 (61, π) 1161.1 (231, σ) 2057.0 (858, σ)
GaOBO ($^1\Sigma$)	8.1(0, π) 8.1 (0, π) 359.1 (102, σ) 538.2 (66, π) 538.2 (66, π) 1129.9 (215,) 2040.7 (924, σ)
InOBO ($^1\Sigma$)	51.2 (0, π) 51.2 (0, π) 303.3 (81, σ) 553.5 (63, π) 553.5 (63, π) 1124.2 (163, σ) 2036.3 (942, σ)

The calculated vibrational frequencies and intensities of the linear MOBO molecules are listed in Table 3. As can be seen, the most intensive IR mode is the terminal B–O stretching mode, which was computed at 2057.0, 2040.7 and 2036.3 cm^{-1} for $AlO^{11}BO$, $^{69}GaO^{11}BO$ and $InO^{11}BO$, respectively. The calculated frequencies should be scaled by 0.980, 0.977 and 0.972 to reproduce the experimentally observed frequencies. This is in accord with the expected accuracy of the B3LYP calculations [27]. The calculated isotopic frequency ratios are also in excellent agreement with the experimental values. Taking the GaOBO molecule for example, the calculations gave ratios of $^{69}GaO^{10}BO/^{69}GaO^{11}BO = 1.0356$ and $^{69}Ga^{16}O^{11}B^{16}O/^{69}Ga^{18}O^{11}B^{18}O = 1.0154$, while the experimental values are $^{69}GaO^{10}BO/^{69}GaO^{11}BO = 1.0350$ and $^{69}Ga^{16}O^{11}B^{16}O/^{69}Ga^{18}O^{11}B^{18}O = 1.0153$.

Beside the terminal B–O stretching mode, the MO–BO stretching mode was predicted to absorb around 1100–1200 cm^{-1} region with appreciable IR intensities. The calculated IR intensity of this mode is about 20% of the intensity of the terminal B–O stretching mode. This mode should be observed if the predicted relative intensities are correct. However, the spectra in this frequency region are quite clean, and no such absorption was observed in this frequency region. We suspect that the IR intensity of the MO–BO stretching mode is overestimated by the DFT/B3LYP calculations.

The MOBO molecules can be regarded as the borates of aluminum (I), gallium (I) and indium (I). The natural atomic charges calculated for MOBO indicate a large amount charge transfer, indicating a mostly ionic bonding. The natural atomic charges of the Al, Ga and In atoms in MOBO are +0.884, +0.875, and +0.918, respectively. Therefore, the MOBO molecules can be denoted as $M^+(OBO)^-$. Consistent with that notion, the B–O stretching frequencies of MOBO are significantly higher than the antisymmetric BO stretching mode of the linear neutral OBO molecule (1299 cm^{-1} for $^{11}BO_2$), and are very close to that of the linear OBO^- anion (1920 cm^{-1} for $^{11}BO_2{}^-$) observed in solid argon [6].

Our experimental observations indicated that the MOBO molecules are most likely formed by the association reactions between metal atoms and BO_2 molecules on annealing, reactions (1)–(3). DFT calculations predicted that these charge transfer reactions are highly exothermic and require no activation energy. BO_2 is the main reaction product from codeposition of laser-evaporated boron and metal atoms with O_2 in excess argon. Sample annealing allowed the BO_2 molecules to diffuse and react with metal atoms to form MOBO:

$$\mathrm{Al} + \mathrm{OBO} \rightarrow \mathrm{AlOBO} \qquad \Delta E = -127.2\ \mathrm{kcal/mol} \tag{1}$$

$$\mathrm{Ga} + \mathrm{OBO} \rightarrow \mathrm{GaOBO} \qquad \Delta E = -112.3\ \mathrm{kcal/mol} \tag{2}$$

$$\mathrm{In} + \mathrm{OBO} \rightarrow \mathrm{InOBO} \qquad \Delta E = -112.6\ \mathrm{kcal/mol} \tag{3}$$

Although weak absorptions due to BO, BOB and other metal oxides were observed on sample deposition, the absence of intermediate absorptions in the mixed $^{16}O_2 + {}^{18}O_2$ experiments excludes the possibility for the formation of MOBO via the BO + MO reactions. Previous investigations have shown that silicon monoxide could form complexes with metal atoms such as Li, Na and Ag [28,29]. However, no obvious absorptions due to species such as MOB were observed in the present experiments.

4. Conclusions

The vibrational spectra and structures of the aluminum, gallium and indium borates MOBO (M = Al, Ga, and In) have been studied by matrix isolation infrared spectroscopy and density functional theory calculations. The MOBO molecules were produced by co-deposition of metal and boron atoms with oxygen molecules at low temperatures in solid argon. The metal borate molecules were identified on the basis of the experimentally observed vibrations with isotopic effects ($^{16}O/^{18}O$ substitutions, and $^{10}B/^{11}B$ and $^{69}Ga/^{71}Ga$ in natural abundance). These metal borate molecules were predicted to have linear geometries with a highly ionic electronic structure.

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