Probing the properties of the (1 1 1) and (1 0 0) surfaces of LaB₆ through infrared spectroscopy of adsorbed CO

Thomas Yorisaki [a,b,c], Aashani Tillekaratne [a], Qingfeng Ge [e], Chuhei Oshima [b,c], Shigeki Otani [d], Michael Trenary [a,*]

[a] Department of Chemistry, University of Illinois at Chicago, 845 W. Taylor St., Chicago, IL 60607, USA
[b] Department of Nano Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
[c] Kagami Memorial Laboratory for Material Science and Technology, Waseda University, 2-8-26 Nishiwaseda, Shinjuku-ku, Tokyo 169-0051, Japan
[d] National Institute for Material Science, 1-1 Namiki, Tsukuba-shi, Ibaraki 305-0044, Japan
[e] Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, USA

ABSTRACT

The adsorption of carbon monoxide on the $LaB_6(1\,0\,0)$ and $LaB_6(1\,1\,1)$ surfaces was studied experimentally with the techniques of reflection absorption infrared spectroscopy and X-ray photoelectron spectroscopy. The interaction of CO with the two surfaces was also studied with density functional theory. Both surfaces adsorb CO molecularly at low temperatures but in markedly different forms. On the $LaB_6(1\,1\,1)$ surface CO initially adsorbs at 90 K in a form that yields a CO stretching mode at 1502–1512 cm^{-1}. With gentle annealing to 120 K, the CO switches to a bonding environment characterized by multiple CO stretch values from 1980 to 2080 cm^{-1}, assigned to one, two, or three CO molecules terminally bonded to the B atoms of a triangular B_3 unit at the (1 1 1) surface. In contrast, on the $LaB_6(1\,0\,0)$ surface only a single CO stretch is observed at 2094 cm^{-1}, which is assigned to an atop CO molecule bonded to a La atom. The maximum intensity of the CO stretch vibration on the (1 0 0) surface is higher than on the (1 1 1) surface by a factor of 5. This difference is related to the different orientations of the CO molecules on the two surfaces and to reduced screening of the CO dynamic dipole moment on the (1 0 0) surface, where the bonding occurs further from the surface plane. On $LaB_6(1\,0\,0)$, XPS measurements indicate that CO dissociates on the surface at temperatures above 400 K.

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1. Introduction

Lanthanum hexaboride has many bulk properties that are similar to those of typical transition metals. One of the most important properties of transition metals is their ability to catalyze numerous important chemical transformations. In the case of heterogeneous catalysis, the key chemical reactions take place on the transition metal surface and so the surface structure and surface chemical properties are of most importance for the use of transition metals as catalysts. One common way to probe the chemical properties of a transition metal surface is through the vibrational frequencies of chemisorbed carbon monoxide. Despite many past studies of the structure of rare earth hexaboride surfaces, the chemical properties of these surfaces have received little attention. In particular, the vibrational spectrum of carbon monoxide adsorbed on a rare earth hexaboride surface has not been previously reported. Here we use reflection absorption infrared spectroscopy (RAIRS) of CO adsorbed on the (1 1 1) and (1 0 0) surfaces of LaB₆ to characterize the nature of the adsorption sites through comparison with the well-known properties of CO chemisorbed on transition metal surfaces.

The hexaborides of trivalent metals have properties usually associated with ceramic materials in that they are hard yet brittle and have very high melting points, and yet they have the high electrical conductivities typical of metals [1]. In contrast, the hexaborides of divalent metals, such as CaB₆, are semiconductors with small band-gaps [2–4]. An explanation for the basic electronic structure of the metal hexaborides was provided by a simple molecular orbital calculation by Longuet-Higgins and Roberts in 1954 [5] who showed that the lattice of interconnected B₆ octahedra requires 20 electrons per B₆ unit to fill its bonding orbitals, whereas only 18 valence electrons are available from the boron atoms alone. Thus the boron lattice requires transfer of two electrons from each metal atom. For trivalent metals, the third valence electron enters into a metallic band imparting metal-like properties, whereas for hexaborides of the divalent metals there is a band-gap between the highest occupied states and the lowest unoccupied states. Despite the approximations on which this simple model is based, the basic description and conclusions reached in Ref. [5] are retained in more recent calculations [3,6,7].

* Corresponding author. Tel.: +1 312 996 0777; fax: +1 312 996 0431.
E-mail address: mtrenary@uic.edu (M. Trenary).

Lanthanum hexaboride has been the subject of numerous surface science studies with most of the work concerned with the properties of the clean surface [8–24] and its interaction with oxygen [25–36]. These studies are in agreement that the $LaB_6(1 0 0)$ surface is terminated in an unreconstructed square lattice of La atoms with the bulk lattice constant of 4.15 Å. In a combined X-ray photoelectron spectroscopy (XPS), inelastic ion scattering spectroscopy (ISS), and low energy electron diffraction (LEED) study [15], it was found that whereas the topmost atomic layer of the (1 0 0) surface consists of La atoms, on the (1 1 1) surface boron atoms lie above the La-atom plane. Since the (1 1 1) surface, like the (1 0 0) surface, shows no reconstruction, it follows that the triangular faces of the B_6 octahedra, which are parallel to the (1 1 1) plane constitute the topmost atomic layer on the $LaB_6(1 1 1)$ surface. These proposed structures of the (1 0 0) and (1 1 1) surfaces of LaB_6 were also supported through comparison of surface phonon dispersion curves measured with high resolution electron energy loss spectroscopy (HREELS) with curves calculated with simple force constant models [37,38]. Fig. 1 shows structural models of the clean surfaces based on these previous studies. In forming the surface, the interoctahedral bonds are broken and on the (1 0 0) surface this leads to a single boron dangling bond oriented along the surface normal through the middle of a square of four lanthanum atoms, whereas on the (1 1 1) surface there are three dangling bonds 55° from the normal along three azimuths 120° apart. The different structures of the (1 0 0) and (1 1 1) surfaces present different types of adsorption sites for reactive chemistry and information on the nature of these sites can be probed through the response of the C–O stretch frequency of adsorbed carbon monoxide.

The relationship between degree of coordination in the bonding of CO to metals and the CO stretch wavenumber is well-known in both metal carbonyl complexes and in CO adsorption on metal surfaces. The extensive literature on this topic has been reviewed by Sheppard and coworkers [39–41]. Thus CO stretch values of 2200–2130 cm^{-1} are assigned to adsorption on positive metal ions whereas lower values are assumed to correspond to adsorption on metals in the zero-oxidation state. Values of 2130–2000 cm^{-1} correspond to CO adsorbed at on-top sites; 2000–1880 cm^{-1} corresponds to CO bridge-bonded to two metal atoms; 1880–1650 cm^{-1} corresponds to CO bonded to three or more metal atoms. In some cases strong coverage dependent blue shifts can move the CO stretch frequency of molecules adsorbed at three-fold hollow sites into the range usually associated with bonding at two-fold sites, which has led to some incorrect assignments, but the general correlation of frequency with adsorption site is still thought to be valid [39]. Cases of more unusual bonding modes, including those where the CO molecules bond in a side-on fashion, where CO stretch frequencies as low as 1251 cm^{-1} have been reported, have been reviewed by de la Cruz and Sheppard [40]. While a comparison of the interaction between CO and the surface La atoms of LaB_6 with CO bonding to a metallic lanthanum surface or with lanthanum carbonyl complexes would be useful, such information is apparently not available. Similarly, there is little information on the bonding of CO to boron surfaces. The lanthanide metals are generally very reactive and based on the behavior of acetylene and ethylene on a clean Gd(0 0 0 1) surface [42], it is reasonable to assume that CO would dissociatively adsorb on a lanthanum surface. Although stable carbonyls of the lanthanides do not appear to exist, the reaction of lanthanide metals with CO in rare gas matrices has been studied and the general correlations between structure and C–O stretch frequencies found for transition metals appear to also apply to the lanthanides. Thus, spectra assigned to $Pr(CO)_6$ and $Nd(CO)_6$ featured C–O stretch values of 1989 and 1990 cm^{-1} [43,44]. Although La was not included in these studies, presumably similar values would be obtained. Thus, despite the abundance of information on the correlations between C–O stretching frequencies and mode of coordination to metal atoms on both surfaces and in complexes, there is scant information in the literature that could be the basis for predicting the results reported here.

In contrast to the numerous surface science studies of rare earth hexaborides and numerous RAIRS studies of CO on transition metal surfaces [45–47], there have not been any previous RAIRS studies of any metal boride surface nor any previous studies of CO interacting with a metal boride surface, even though there is no fundamental reason why the technique cannot be applied to such surfaces. Although general equations are available [48] for estimating the reflectivity change for a given adsorbate on a particular metal substrate, their use requires knowledge of the optical constants of the
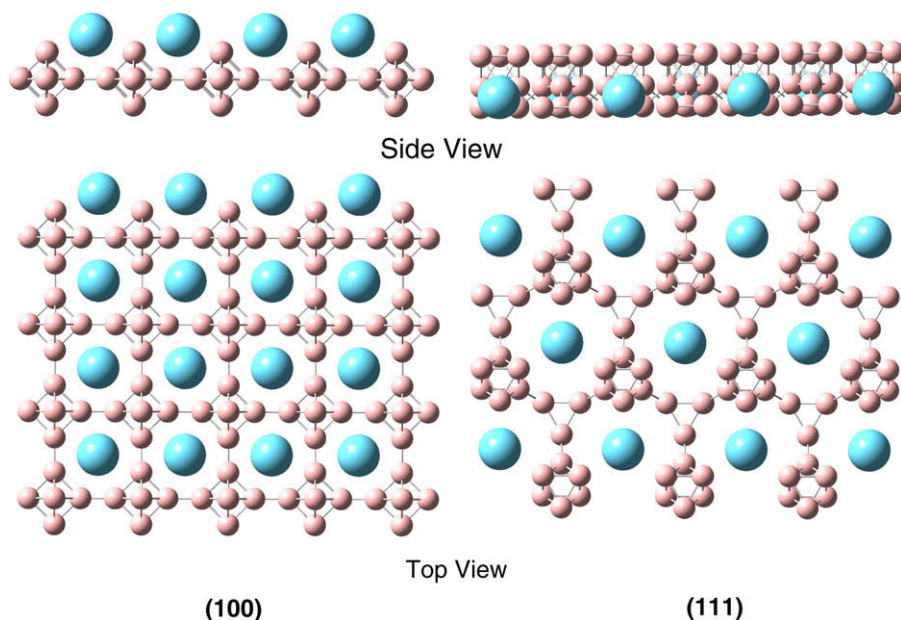

Side View

Top View

(100)   (111)

Fig. 1. Side and top views of the structure of the (1 0 0) and (1 1 1) surfaces of LaB_6. (This figure and several others appear in color in the on-line version.)