Ab initio versus CNDO Potential Surface Calculations for Li$_2$O and Al$_2$O

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Potential surfaces for Li$_2$O and Al$_2$O have been calculated by an ab initio SCF–LCAO–MO method and by the semiempirical CNDO method. For both molecules the semiempirical methods incorrectly imply unreasonable structures with very acute apex angles and very long bond distances—rather more like diatomic Li$_2$ or Al$_2$ molecules with O-atoms attached to their bonds. Our ab initio treatment does correctly predict a symmetrical linear configuration for Li$_2$O with bond distances in excellent agreement with experiment. This method also predicts a linear symmetrical structure for Al$_2$O, in agreement with experimental gas phase measurements but in disagreement with matrix-isolation studies.

Key words: Potential surfaces – Li$_2$O–Al$_2$O – Ab initio versus CNDO potential surface calculations

Introduction

Although semiempirical molecular orbital methods are being used extensively for calculating various molecular properties, it is apparent that the results of such calculations may be quite misleading in certain cases [1]. However, it is generally conceded that the geometrical configuration is the most reliable molecular property calculable by semiempirical methods, and in fact, qualitative agreement of such calculations with experiment is most often obtained. For example, the semiempirical CNDO (Complete Neglect of Differential Overlap) and INDO (Intermediate Neglect of Differential Overlap) methods give quite satisfactory angular geometry predictions for a variety of molecular types, in particular, for “normal” AB$_2$-type molecules [2], although often the predicted bond distances are in significant error. Our CNDO energy contour diagrams (potential surfaces) for H$_2$O and F$_2$O are displayed in Fig. 1. These diagrams correctly predict $C_{2v}$ geometries with apex angles of 104.2° and 106.8°, respectively, as compared with the observed 104.5° and 103.3° angles. Generally, as here, the CNDO calculated bond distances are somewhat in error.

In special cases where the molecules have “anomalous” structures, certain of the semiempirical methods apparently cannot cope even with the problem of geometry prediction [3]. One illustration of a simple molecule with anomalous geometry is the dilithium oxide molecule, Li$_2$O. It has been concluded from mass spectrometric and infrared matrix-isolation studies [4] and from electric deflection measurements [5] that Li$_2$O molecules in the vapor phase are linear symmetrical with Li–O distances estimated to be 1.59 Å and 1.55 Å,
Fig. 1. CNDO energy contour diagrams for H$_2$O and F$_2$O

respectively. In a subsequent electron diffraction study of the vapor, the Li–O distance was determined to be 1.60 ± 0.02 Å [6]. This linear structure for the Li$_2$O molecule requires an apex angle considerably larger than the "normal" angle about an oxygen atom (H$_2$O, 104°27'; F$_2$O, 103°18'; Me$_2$O, 111°37'; O$_3$, 116°48'; etc.). Such gross differences from the normal angle have been attributed to the presence of strongly electropositive ligands [7], in which case, "ionic repulsions overcome the lone-pair repulsions". An earlier SCF calculation on Li$_2$O corroborated the highly ionic linear structure but predicted a bond distance of 1.65 Å [8].

Another related molecule which may also have an anomalous geometry is dialuminum oxide (aluminum suboxide), Al$_2$O. Electric-deflection measurements were interpreted as favoring a $D_{x'y'y'}$ linear structure [5], although the conclusions in this case were not considered unambiguous because of the possibly small Al–O bond moment. Infrared studies of gaseous Al$_2$O further indicated that the molecule was linear [9]. However, infrared spectral measurements of Al$_2^{16}$O and Al$_2^{18}$O vapors trapped in rare gas matrices [10, 11], seemed to establish a bent $C_{2v}$ structure with an apex angle of about 145°. The Al–O distance was estimated to be 1.65 – 1.66 Å using the Laurie-Hershbach relation [12]. Further studies of the infrared spectra of Al$_2$O molecules isolated in rare gas matrices, which find the $v_2$ bending mode at a quite high frequency, suggest the occurrence of a metal-metal bond resulting in a ring-type structure [13]. In any case, although the structure of gaseous Al$_2$O has not been well established experimentally, the apex angle is apparently considerably larger than normal, so the Al$_2$O molecule may be adjusted to have an anomalous