THE ROTATIONAL SPECTRUM AND DYNAMICAL STRUCTURE OF LiOH AND LiOD: A COMBINED LABORATORY AND AB INITIO STUDY

ALDO J. APPONI, LUCY M. ZIURYS, *Department of Chemistry, Department of Astronomy, and Steward Observatory, The University of Arizona, Tucson, Arizona 85721*; KELLY J. HIGGINS, and WILLIAM KLEMPERER, *Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138.*

Millimeter wave spectroscopy and *ab initio* calculations are used to explore the potential energy surface (PES) of LiOH and LiOD with particular emphasis on the bending states and bending potential. New measurements extend the observed rotational lines to $J = 7 \leftarrow 6$ for LiOH and $J = 8 \leftarrow 7$ for LiOD for all bending vibrational states up to (03^30). The full three-dimensional PES is calculated on a grid of 1040 points at the CCSD(T) level using a quadruple-ζ quality basis set and including the effects of core electron correlation. The dipole moment surface is calculated at the MP2 level on the same grid of points with the same basis and core electron correlation. Rovibrational energy levels, geometric expectation values, and dipole moments are calculated using the DVR3D program suite of Tennyson and coworkers.[a,b] Agreement between calculation and experiment is superb, with predicted B_v values within 0.3% of experiment, D_J values within 0.6%, q_l values within 0.7%, and dipole moments within 0.9%. The PES also predicts a change from a linear minimum energy configuration at equilibrium to a bent minimum energy configuration starting at an Li-O bond length of 1.7866 Å and culminating in a 104° bond angle at an Li-O bond length of 3 Å. Implications of this study in terms of LiOH bonding and its relationship to bent HOH and linear LiOLi will be explored.[c]

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[a] J. Tennyson, J. R. Henderson, and N. G. Fulton, Computer Phys. Comm. 86, 175 (1995).

[b] J. Tennyson, M. A. Kostin, P. Barletta, G. J. Harris, J. Ramanlal, O. L. Polyansky and N. F. Zobov, Computer Phys. Comm. (in press).

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