

## DETERMINATION OF THE Li-Ar $X\Sigma$ INTERACTION POTENTIAL FROM LASERSPECTROSCOPIC DATA

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The absorption spectrum of LiAr due to the  $A^2\Pi \leftarrow X^2\Sigma$  transition was recorded between 14720 and 14895  $\text{cm}^{-1}$  observing the laser-induced fluorescence for detection. The LiAr molecules were produced by supersonic expansion of a mixture of Li vapor and Ar through a nozzle into a vacuum. Up to now, rovibrational quantum numbers could successfully be assigned to about 750 and 120 lines due to the isotopomers  $^7\text{LiAr}$  and  $^6\text{LiAr}$  with relative abundance of 92.4% and 7.6%, respectively. The lines correspond to vibrational transitions between  $v'' = 0\dots 2$  of  $X\Sigma$  and  $v' = 5\dots 8$  of  $A\Pi$ .

As in our previous work [1] the eigenvalues, being calculated from the interatomic potential in a quantum-mechanical approach, were fitted to the observed energy values of rovibrational levels by varying the parameters of the potential. For the  $X\Sigma$  state the observed energies could be reproduced within experimental error of 0.01  $\text{cm}^{-1}$  by using a Thakkar or a Hartree-Fock-Dispersion function [1] with 6 parameters as an analytical expression for the interatomic potential. Our preliminary values for equilibrium distance and well-depth of the  $X\Sigma$  state are  $R_e = 4.90(2)$  Å,  $D_e = 42.5(1.5)$   $\text{cm}^{-1}$ . A corresponding analysis of the  $A^2\Pi$  states is presently under way. In addition, the spectral distribution of the fluorescence light has been observed which will provide information on the repulsive part of the  $X\Sigma$  interaction potential.

TORSIONAL SPLITTING IN THE  $2\nu_9$   
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In addition to being important from the atmospheric point of view, nitric acid is also interesting from the theoretical point of view, since it displays a large amplitude motion consisting of an internal rotation of the OH group with respect to the  $\text{NO}_3$  group. This large amplitude motion, corresponding to the  $\nu_9$  mode, splits the rotational levels into two sublevels, but only one sublevel out of two is populated in the normal species. Evidence for this large amplitude motion was found in the  $\nu_9 = 2$  and  $\nu_9 = 3$  vibrational states.<sup>1-2</sup>

Using already published data,<sup>3</sup> a reanalysis of the  $\nu_5$  and  $2\nu_9$  bands of nitric acid has been carried out. In this analysis, the large amplitude motion was accounted for as well as the rotational dependence of the corresponding tunneling splitting.<sup>4</sup> This rotational dependence cannot be expressed as a polynomial expansion in terms of angular momentum operators, and in the analysis this allowed us to discriminate between the effects due to centrifugal distortion and those due to the large amplitude motion. Since these latter effects are smaller than the experimental resolution,<sup>3</sup> information on the tunneling splitting was extracted from those lines which are unblended and which are shifted by the tunneling. The analysis yields a value of  $0.0013(1) \text{ cm}^{-1}$  for the tunneling splitting, which is consistent with the high resolution measurements.<sup>1</sup> The values for the parameters involved in the rotational dependence have also been determined and compare favorably with those obtained from the equilibrium structure.

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THE STARK EFFECT FOR THE WATER MOLECULE  
CALCULATED FROM FIRST PRINCIPLESMarkus Mengel\* and Per Jensen\*,†

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We report here the development of a theoretical method to calculate Stark splittings and state dependent dipole moments for a triatomic molecule based on the MORBID approach [P. Jensen, *J. Mol. Spectrosc.* **128**, 478-501 (1988)]. The Stark parameters are obtained directly from the potential energy surface and dipole moment functions of the molecule. The transformation of the dipole moment from molecule fixed to space fixed axes is carried out by means of irreducible tensor formalism. We apply the new method to H<sub>2</sub>O since for this molecule, we have an accurate potential energy surface [P. Jensen, *J. Mol. Spectrosc.* **133**, 438-460 (1989)] obtained by fitting to experimental data, and a high-quality *ab initio* dipole moment surface [U.G. Jørgensen and P. Jensen, *J. Mol. Spectrosc.* **161**, 219-242 (1993)]. The results of calculations on the basis of these input data are in good agreement with experiment. However, we have improved this agreement further by refining the dipole moment surfaces in least squares fits of experimental Stark data, in particular of the very accurate MBER measurements by Shostak *et al.* [S. Shostak, W. Ebenstein and J.S. Muentner, *J. Chem. Phys.* **94**, 5875-5882 (1991)]. With the refined dipole moment surface, we have calculated state dependent dipole moment values. The variation of these values with vibrational excitation is in close agreement with that found in the experimentally derived values of Shostak *et al.*