AB INITIO MULTI-REFERENCE PERTURBATION THEORY STUDY ON THE LiRb MOLECULE

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Cold and ultracold polar molecules offer prospects for the realization of new forms of quantum matter with possible applications to quantum information and to precision measurements [1]. One of the possibilities of obtaining of molecular quantum matter with controlled properties is the transferring of the polar diatomic molecules to the ground rovibronic state by initial optical excitation into the overlying rovibronic states with specific forms of electronic terms. In this case for the high efficiency of excitation and subsequent relaxation of the molecular system it is required knowledge of the exact forms of the potential energy curves (PECs) of the combining electronic states. The construction of exact empirical terms is performed on the basis of the analysis and interpretation of high-resolution rovibronic spectra, and may be based on *ab initio* potential curves. The knowledge of the exact PECs also allows to define the important spectra-energetic characteristics of molecules and the macroscopic physical properties of rarefied gases. So within the framework of the Chapman-Enskog kinetic theory of gases [2], it is possible to obtain important transport properties, for example, coefficients of diffusion, viscosity, thermal conductivity, etc., of gases and liquids.

The diatomic polar molecule LiRb is a typical example of the above-mentioned compounds. In this study, the SA-CASSCF(4,10)/XMCQDPT2 [3] calculations of the low-lying singlet and triplet states of the LiRb molecule performed (Fig. 1). The calculations were carried out in two stages in the wide range of internuclear distances taking into account static and dynamic part of correlation energy. The TZ-basis sets and Stuttgart RSC ECP (for Rb atom) have been used in calculations. The results of our calculations of the spectroscopic parameters of the LiRb's ground state $X^1\Sigma^+$ (R_e = 3.4508 Å, D_e = 5926.7 cm^{-1},) very well agree with experimental data (R_e = 3.4661 Å, D_e = 5927.9 cm^{-1} [4]). This is the best agreement among all previously performed for LiRb molecule *ab initio* calculations.

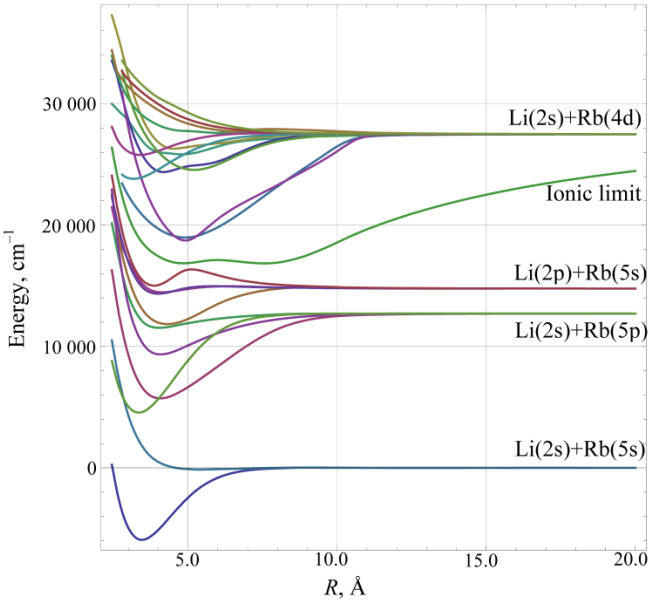

Fig. 1. The low-lying singlet and triplet states of the LiRb at the CASSCF(4,10)/XMCQDPT2 level of theory.

On the basis of the kinetic theory of gases and calculated potential for the ground state the transport properties of a diluted two-component Li-Rb gas were defined. At first stage the extrapolation of PEC into the region of small internuclear distances was made. Then consequent calculations of distance of the closest approach, the angle of deflection and the collisional cross-section were performed to evaluate the reduced collision integrals, through which coefficients of diffusion, viscosity and thermal conductivity are determined. These transport properties are obtained as functions of pressure and temperature.

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[1] O. Dulieu, C. Gabbanini, The formation and interactions of cold and ultracold molecules: new challenges for interdisciplinary physics, Rep. Prog. Phys. **72**, 086401 (2009).
[2] O. Hirschfelder, C.F. Curtiss, R.B. Bird, *Molecular theory of gases and liquids* (Wiley, New York; Chapman Hall, London, 1954).
[3] A.A. Granovsky, Extended multi-configuration quasi-degenerate perturbation theory: the new approach to multi-state multi-reference perturbation theory, J. Chem. Phys. **134**, 214113 (2011).
[4] M. Ivanova, A. Stein, A. Pashov, H. Knöckel, E. Tiemann, The $X^1\Sigma^+$ state of LiRb studied by Fourier-transform spectroscopy, J. Chem. Phys. **134**, 024321 (2011).