

COUPLED CLUSTER STUDY OF SPECTROSCOPIC CONSTANTS OF THE ALKALI METAL DIATOMICS: GROUND AND THE SINGLET EXCITED STATES OF Na₂, NaLi, NaK, and NaRb

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A newly implemented two-determinant coupled cluster method including single and double excitation operators (TD-CCSD) is applied to calculations of spectroscopic constants of alkali metal diatomics. Method is based on Hilbert space approach of Jeziorski and Monkhorst [1], exploiting *C-conditions* [2, 3, 1] for incomplete model space. Implementation represents a continuation of previous works [4, 5].

The equilibrium bond length, harmonic vibrational frequency, anharmonicity, the dissociation energy and excitation energies are derived from the potential curves calculated for the ground state $X^1\Sigma_g^+$ and the two singlet mono-excited states, $A^1\Sigma_u^+$ and $B^1\Pi_u$ of Na₂ as well as for the ground $X^1\Sigma^+$ and the singlet excited $A^1\Sigma^+$ and $B^1\Pi$ states of the heteronuclear NaLi, NaK, and NaRb molecules. For example, for Na₂ we obtain $R_e = 3.677$ Å, 3.424 Å and $\omega_e = 115.0$ cm⁻¹, 125.5 cm⁻¹ for A and B states, respectively (exp.: $R_e = 3.638$, 3.423 Å, $\omega_e = 117.3$, 124.4 cm⁻¹). Spectroscopic constants and excitation energies agree reasonably well with experiment. Our results demonstrate that the relatively simple CCSD method for the excited states represented by two-reference determinants is a viable technique. The computer time needed for an excited singlet state is practically identical to the time which a standard single-determinant-based CCSD calculation takes.

References

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