RESONANCE ENHANCED TWO-PHOTON IONIZATION (RE2PI) SPECTRUM OF THE 520 NM SYSTEM OF RbCs

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The rovibrational spectrum of RbCs molecule in the range of 520 nm is observed by the resonance enhanced two-photon ionization (RE2PI) method. A very cold pulsed molecular beam that contains RbCs, Rb_2, Cs_2, etc is generated by a high temperature pulsed nozzle. Only $RbCs^+$ ion could be detected using the time-of-flight (TOF) mass spectrometer (mass resolution $\sim$ 1300). Vibrational bands ($v' = 6 \sim 31$) are rotationally resolved by the high resolution dye laser with an intracavity etalon (laser resolution ~ 0.02 cm^{-1}). The excited electronic state is assigned to the $5\ ^1\Sigma^+$ state that dissociates into Rb(5s $^2S_{1/2}$) + Cs(7s $^2S_{1/2}$). By the pseudopotential calculation, the $5\ ^1\Sigma^+$ state has adiabatic potential curve with a shelf as a result of the avoided crossing with ionic pair state at long internuclear distances. Observed in the Franck-Condon region, however, the ΔG_v curve shows slightly positive curvature for $v' > 20$, which may result from the avoided crossing with the $6\ ^1\Sigma^+$ state at ~ 6 Å.

By the selection rules of $\Delta J = \pm 1$ for $^1\Sigma \rightarrow\ ^1\Sigma$ transitions, only P and R lines are observed. The rotational constants, B_v, and the vibrational term value, T_v, are determined from the analysis of the rotationally resolved spectra. From the vibrational energy level spacing, ΔG_v, the spectroscopic parameters for the $5\ ^1\Sigma^+$ state are determined as $T_e = 18560.12(8)$ cm^{-1}, $\omega_e = 40.83(1)$ cm^{-1}, and $\omega_e x_e = 0.2465(6)$ cm^{-1}.

The dissociation energy, D_e, is 3811.5 cm^{-1}. Measured isotope shifts confirm the absolute vibrational numbering. The B_e and α_e obtained from the B_v vs. v plot are 0.013468(8) cm^{-1} and $7.48(4) \times 10^{-5}$ cm^{-1}, respectively. Using these molecular constants, potential energy curve of the $5\ ^1\Sigma^+$ state is constructed by the RKR method.