SESSION BL 2

TITLE	Firefly bioluminescence: molecules and mechanisms		
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ABSTRACT	The spectrochemistry of oxyluciferin is exceedingly complex. Even though the complex chemistry of firefly oxyluciferin has spurred extensive experimental and theoretical studies, the photophysics of this 'phantom molecule' remains poorly characterized. It can exist in six different forms as a result of ionization of two hydroxyl groups and the keto-enol tautomerism of the 4-thiazolone subunit. The intricate triple dynamic chemical equilibrium in solution is strongly affected by the solvent, pH, and specific interactions with bases. Moreover, the spectral properties of each chemical form could be additionally affected in the enzyme by the nature of the active site such as polarity, presence of additional ions, and pi-pi stacking. Historically, the phenolate-keto species has been considered the most viable form for the emitting state. However, recent studies have shown that the enol tautomer should not be excluded as emitting species that is generated in the excited state. Moreover, ultrafast spectroscopic results have indicated possible excited-state proton transfer (ESPT) from either of the two hydroxyl groups. Experimental and theoretical studies of the firefly luciferin (the reaction precursor) have shown that the photoluminescence pathways of this closely related molecule also depend strongly on pH and excitation wavelength. This session will combine talks from experimentalists and computational chemists in an attempt to reach a common ground for the mechanism of firefly bioluminescence.		
KEYWORDS	Firefly, bioluminescence, oxyluciferin, calculations, spectroscopy		