フォノンの放出・吸収過程としての内部転換：振電相互作用定数とエネルギーギャップの依存性

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Internal Conversion as a Phonon-Emission/Absorption Process: Role of Vibronic Couplings and Energy Gap

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An analytical expression for the rate constant of internal conversion (IC) was derived based on the crude adiabatic representation. All vibrational modes were considered to be on an equal footing in the rate constant expression. Based on this expression, we investigated the role of vibronic couplings and electronic energy gap in IC processes, using 9-fluorenone as an illustrative example. Vibrational modes with strong off-diagonal vibronic coupling constants (VCCs) give rise to non-radiative transitions. In contrast, vibrational modes with strong diagonal VCCs constitute the final vibronic states that accept the excess electronic energy between the initial and final electronic states. Therefore, vibrational modes are classified into promoting and accepting modes based on their roles. We identified important promoting modes responsible for one-phonon emission and accepting modes that contribute greatly to the final state. A Franck-Condon envelope, which describes the density of final vibronic states, explains the dependence of the rate constant on the electronic energy gap. VCC can be visualized as a spatial distribution of its density form, i.e., vibronic coupling density (VCD). The VCD concept is expected to facilitate the design of functional molecules with IC processes understood in terms of electronic states and vibrational modes.

Keywords： *Nonradiative Transition; Internal Conversion; Vibronic Coupling*

粗断熱表現を用いたフェルミの黄金律に基づき、分子の全振動モードを考慮した内部転換速度定数の解析的表式を導出した 1,2)。内部転換は振電相互作用を駆動力としたフォノン放出過程とみなせる。得られた解析的表式により、振電相互作用の選択則に基づきながら、振動モードをフォノン放出に関与するモード（促進モード）と電子励起エネルギーを受け取るモード（受容モード）に分類することができる。また、終振電状態の状態密度を表すフランク・コンドン包絡線により、速度定数のエネルギーギャップ依存性を説明することができる。粗断熱表現を用いることで、振電相互作用の起源を振電相互作用密度 3)により明らかにし、内部転換を制御した分子設計に応用することが可能である。計算によって得られた９ーフルオレノンの内部転換速度定数は実験値を良く再現した。

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