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Entitled

Molecular Geometry Changes in Some Carbonyls and Aromatic Rings upon Electronic Excitation: Herzberg-Teller Vibronic Coupling and Unitary Duschinsky Rotation

by

Maryam Mohammed Al Sakkaf

Faculty Advisor

Prof. Mohamad Toutounji, Department of Chemistry

College of Science

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Abstract

The common assumption in probing the dynamical motion of molecules is that the molecular electronic activity depends weakly on vibrational coordinates on electronic excitation. Therefore, electron-vibration interaction, which is known as vibronic coupling (VC), may be ignored. The Herzberg-Teller theory of vibronic coupling (HTVC) is a breakdown of the Born-Oppenheimer approximation (BOA) since nuclear and electronic degrees of freedom can no longer be separated. The inclusion of a single quantum of a non-totally symmetric vibrational mode changes the overall symmetry of the state and permits the transition. Often, this assumption may be invalid, especially in carbonyl and aromatic compounds. This thesis will use both quantum mechanics and electronic structure theory of molecules to probe the breakdown of this assumption in carbonyls (CH_2CO, CH_3CHO, andCH_3COCH_3) and aromatic carbonyl compounds (C_6H_5CHO and $C_6H_5COC_6H_5$). This work will investigate the extent to which (HTVC) is significant by looking at nuclear coordinates deformation and electronic density redistribution upon electronic excitation. Non-totally symmetric vibrations are important to identify the coupled electronic states whereby intensity is borrowed from nearby electronic states in case of forbidden electronic transitions by symmetry in the FC region. This electronic density redistribution distortion may be due to the Duschinsky matrix (DM) and HTVC interaction renders information on how the transition moment varies as the molecular geometry changes, giving rise to the non-Condon regime. This coupling should be probed to see if it is caused by orbital interaction and this interaction would give rise to non-adiabatic coupling. This molecular geometry alteration is so important for probing and hence understanding vibration-electron coupling in polyatomic molecules.

Keywords: Born Oppenheimer, Vibronic coupling, Duschinsky rotation and molecular, Herzberg-Teller effect and molecular geometry.