Franck–Condon simulation of photoelectron spectroscopy of acridine: comparison between simulation and experiment

M.Samimi1, M. Dehestani2

1.Department of Chemistry, Science and Research Branch, Islamic azad university, Tehran, Iran
2.Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, Iran
Email:samimi_marziyeh@yahoo.com)

Abstract

A theoretical method to calculate multidimensional Franck–Condon factors is described and used to simulate the photoelectron spectrum of the anion acridine(AD^-). Negative ion photoelectron spectroscopy was employed to investigate the electronic structure of the acridine molecular anion and its monohydrated anion in the gas phase. Geometry optimizations and harmonic vibrational frequency calculations have been performed on the X^1A1 state of AD and X^2A1 state of AD^- are obtained by employing an iterative Franck–Condon analysis procedure in the spectral simulations.

Keywords:AcridineAb initio calculations, Franck–Condon factors , Photoelectron spectrum.

Introduction

The Franck-Condon (FC) analysis can be performed when vibrational structure is observed in an electronic band. Valence ionization energy ofanion acridine (AD^-) and the first ionization energy of acridine (AD) have been obtained by photoelectron spectroscopy [1,2]. The reactive molecule acridine have been studied using photoelectron spectroscopy including techniques of time-averaging and spectrum-stripping . In the present work, we have carried out spectral simulations of the photoelectron of acridine, employing FC factors. This is based on the harmonic oscillator model and includes Duschinsky rotation. We have performed *ab initio* calculations to evaluate the required parameters of our model using the Gaussian 03 suite of quantum chemical codes. Geometries and adiabatic vibrational frequencies for ground electonic states of acridine and anion acridine have been obtained.

Theoretical method

The theoretical method implemented in the present study has been worked out previously in Ref. [4].In the approximation of a slowly varying electronic transition moment, and of the separability of the electronic and vibrational parts of the wavefunctions, the transition intensities are proportional to the square of the electronic transition moment. With this assumption that the lower and upper harmonic potential surfaces are displaced, distorted and rotated (i.e. the Duschinsky

transformation), N-dimensional FC integrals between displaced distorted-rotated harmonic potential surfaces by employing the generating functions method are given by [4]

$$\langle \nu''_1\nu''_2 0''_3 \ldots 0''_N | \nu'_1\nu'_2 0'_3 \ldots 0'_N \rangle = \langle 0''_1 \ldots 0''_N | 0'_1 \ldots 0'_N \rangle \times \prod_{j=1}^{2} (-1)^{\nu''_j} (\nu''_j! \nu'_j!)^{1/2} \sum_{k_1=0} \cdots \sum_{k_6=0} \frac{(-\beta_{12})^{k_1}}{k_1!} \frac{(-2R_{11})^{k_2}}{k_2!}$$

$$\times \frac{(-2R_{12})^{k_3}}{k_3!} \frac{(-2R_{21})^{k_4}}{k_4!} \frac{(-2R_{22})^{k_5}}{k_5!} \frac{(-\alpha_{12})^{k_6}}{k_6!} \times \left\{ \frac{(\beta_{11}/2)^{(\nu''_1-k_1-k_2-k_3)/2}}{(\nu''_1-k_1-k_2-k_3)!} H_{\nu''_1-k_1-k_2-k_3}[\beta_{11}^{-1/2}(R\delta)_1] \right\}$$

$$\times \left\{ \frac{(\beta_{22}/2)^{(\nu''_2-k_1-k_4-k_5)/2}}{(\nu''_2-k_1-k_4-k_5)!} H_{(\nu'_2-k_1-k_4-k_5)}[\beta_{22}^{-1/2}(R\delta)_2] \right\} \times \left\{ \frac{(\alpha_{11}/2)^{(\nu'_1-k_2-k_4-k_6)/2}}{(\nu'_1-k_2-k_4-k_6)!} H_{(\nu'_1-k_2-k_4-k_6)}\{\alpha_{11}^{-1/2}[(E-P)\delta]_1\} \right\}$$

$$\times \left\{ \frac{(\alpha_{22}/2)^{(\nu'_2-k_3-k_5-k_6)/2}}{(\nu_2-k_3-k_5-k_6)!} H_{(\nu_2-k_3-k_5-k_6)}\{\alpha_{22}^{-1/2}[(E-P)\delta]_2\} \right\}$$

where $(v''_1 \ldots v''_N)$and $(v'_1 \ldots v'_N)$refer to the vibrational quantum numbers of the two electronic states initial and final, respectively, $\delta=\Gamma'^{1/2}D$ is the N-dimensional vector of the reduced displacements $\{\gamma_j'^{1/2} D_j\}$, and Γ' is an $N\times N$ diagonal matrix of the reduced frequency $\gamma'_j = \omega'_j/\hbar$, E is an $N\times N$ unit matrix, $H_{\alpha'_j}(x)$ is the Hermite polynomial, and $N\times N$ symmetric matrices P and Q and the $N\times N$ matrix R are defined by

$$\mathbf{P} = \mathbf{\Gamma}''^{1/2}\mathbf{J}\mathbf{G}^{-1}\mathbf{J}^{+}\mathbf{\Gamma}'^{1/2} \quad \mathbf{Q} = \mathbf{\Gamma}''^{1/2}\mathbf{G}^{-1}\mathbf{\Gamma}''^{1/2} \quad \mathbf{R} = \mathbf{\Gamma}''^{1/2}\mathbf{G}^{-1}\mathbf{J}^{+}\mathbf{\Gamma}'^{1/2}$$

$\mathbf{G} = \mathbf{\Gamma}'' + \mathbf{J}^{+}\mathbf{\Gamma}'\mathbf{J}$, $\alpha_{ij} = (\mathbf{E}-2\mathbf{P})_{ij}$, $\beta_{ij} = (\mathbf{E}-2\mathbf{Q})_{ij}$, and

$$\langle 0''_1 \ldots 0''_N | 0'_1 \ldots 0'_N \rangle = (\det \mathbf{\Gamma}''^{1/2}\mathbf{\Gamma}'^{1/2}\boldsymbol{Q})^{1/2} 2^{N/2} exp\left[-\frac{1}{2}\boldsymbol{\delta}^{\dagger}(\boldsymbol{E}-\boldsymbol{P})\boldsymbol{\delta}\right]$$

molecules and anion were assumed to be displaced, distorted, and rotated harmonic oscillators, were evaluated using the method developed by Islampour *et al*.[4] that is briefly described in theory part.The Duschinsky matrix (J) and the vector of dimensionless displacements (D) between the normal modes of the ground states of the molecules and anion should be determined before one can evaluate FC integrals. These are given as [6]:

$$J=[MS'V'^{-1/2}]^{\dagger}ZSV^{-1/2}$$

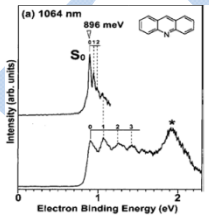
$$D=0.1723[MS'V'^{-1/2}]^{\dagger}R$$

where M is the 3N×3N diagonal matrix with the atomic masses on the diagonal, S′ and S are the 3N×3N-6 matrices of the Gaussian program normal mode output the final state and the initial state in the transition, respectively. V (V') are 3N-6×3N-6 diagonal matrices of the reduced masses of each mode at the electronic state lower (upper). Z is a unit matrix for most molecules of C_{2V} or higher symmetry. R is the N-dimensional vector of the change in equilibrium geometry between the lower to the upper electronic state in Cartesian coordinate on the molecular center of mass

Results and Discussions

The optimized geometric parameters (the bond lengths and angles) and computed harmonic vibrational frequencies for the neutral and anion species of acridineobtained in this work . These tables contain the *ab initio* results obtained with the MP2 and DFT methods. Noticeable is the very good agreement between the experimental data [3] and those that are obtained at the B3LYP/6-31+G(3d,2p) level of theory for neutral acridine[1, 3].

We have used the B3LYP/6-31+G(3d,2p) *ab initio* results for neutral and anion species of acridine, respectively.Tocalculate the Duschinsy matrices(J),and dimensionless displacements (D) between the normal modes of the neutral and anion ground states of the acridine species. The nuclear displacement for the nontotally symmetric mode b_2 is zero. These data were then used to simulate the photoelectron spectra. All of the calculations were carried out using *Mathematica* programs [3].



Figural. 1. .The experimental photoelectron spectrum of AD^-(from reference [4]).and the simulation spectrum of AD^-.

References

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