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Simulation of the photodetachment spectrum of the pyrrolide anion

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This paper is dedicated to Professor Lorenz S. Cederbaum on the occasion of his 60th birthday.

Abstract

The photodetachment spectrum of the pyrrolide anion, $C_4H_4N^-$, has been measured recently [A.J. Gianola, T. Ichino, R.L. Hoenigman, S. Kato, V.M. Bierbaum, W.C. Lineberger, J. Phys. Chem. A 108 (2004), 10326]. The band associated with the 1^2A_2 ground state of the pyrrolyl radical, C_4H_4N, can be identified in the spectrum by its resolved vibrational progression. In contrast, the second band, belonging to the 1^2B_1 first excited state of pyrrolyl, is very weak, broad, and unresolved, which suggests the presence of strong vibronic interaction effects. We have performed a theoretical study of the spectrum in the framework of the linear vibronic coupling model, using *ab initio* calculated parameters. It is shown that a 1^2B_1–1^2A_2 conical intersection is responsible for the unresolved part of the spectrum. The potential-energy surfaces of the 1^2A_2 and 1^2B_1 states of pyrrolyl as a function of the a_1 and b_2 ground state normal coordinates of pyrrolide have been computed with the MRCI/aug-cc-pVDZ method. Only the b_2 modes can couple the involved electronic states in first order. Five totally symmetric modes (a_1 symmetry) and four modes of b_2 symmetry have been identified as the vibronically most active tuning and coupling vibrations, respectively. Model Hamiltonians for the description of the dynamics in the coupled vibronic manifold of the 1^2A_2 and 1^2B_1 states, including different subsets of these nine modes, have been constructed. The simulated spectra predict a 1^2A_2 band with sharp peaks and a very diffuse 1^2B_1 band stretching from 2.6 to 3.3 eV with a maximum close to 3.0 eV. The calculated spectra are in good agreement with experiment. Reasons for the unexpectedly low intensity of the 1^2B_1 band such as an extremely short lifetime of 1^2B_1 vibronic levels or very different photodetachment cross sections for the 1^2A_2 and 1^2B_1 states are discussed.

Keywords: Pyrrolide anion; Pyrrolyl radical; Vibronic coupling; Conical intersection; Photodetachment spectroscopy

1. Introduction

In recent years, the photochemical processes occurring in aromatic amino acids and nucleic bases have been of great interest because they are the most important building blocks of living beings [1–3]. In particular, pyrrole, C_4H_5N, and its derivatives have emerged as interesting prototype molecules for the exploration of photoinduced excited-state dynamics both from the point of view of experimental observations and theoretical calculations.

In many previous studies it has been clarified that UV absorption of these systems is followed by nonadiabatic transitions between excited electronic states and the electronic ground state that lead to ultrafast internal conversion. This mechanism can possibly explain an important property, the so called "photostability", of the building blocks, which protects the living matter from dangerous photoreactions [1–3]. For pyrrole, it also has been found that the detachment of fast hydrogen atoms can be a result of the photoinduced dynamical processes, which lead to hydrogen and pyrrolyl radical, C_4H_4N [4–6]. Although there have been extensive investigations concerning the photoinduced dissociation of pyrrole [4–11], there is still quite limited information about its dissociation product, the pyrrolyl radical. Undoubtedly, knowledge of the prop-

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erties of the pyrrolyl radical will provide us with a more complete picture of the photoinduced dynamics of pyrrole, but until now it is difficult to detect this radical directly in spectroscopic experiments.

In fact, the electronic structure of the pyrrolyl radical is a very interesting topic. The pyrrolyl radical can be considered as a prototypical system for the improvement of the understanding of the basic properties of aromatic heterocyclic radicals. It may be possible to extrapolate some of the results for this simple system to more complex radicals of biological relevance.

It is worthwhile to note that the pyrrolyl radical is isoelectronic with the furan radical cation. A detailed analysis of the vibronic coupling of the 1^2A_2 and 1^2B_1 electronic states of the latter species has been given by Trofimov et al. [12].

Recently, the 363.8 nm (3.408 eV) photoelectron spectrum of the pyrrolide anion, $C_4H_4N^-$, has been measured [13]. This photodetachment spectrum provides direct information on the electronic structure of the pyrrolyl radical. The experimental spectrum displays remarkable differences between the transitions from the 1^1A_1 ground state of the pyrrolide anion to the 1^2A_2 ground state and to the 1^2B_1 first excited state of the pyrrolyl radical, respectively. The 1^2A_2 band shows a partly resolved vibrational structure, which indicates that the 1^2A_2 state is a bound state. The 1^2B_1 band, on the other hand, could not be clearly identified in the experimental photodetachment spectrum [13]. The questions arising from this observation will be addressed in the present work.

Previous *ab initio* calculations have already confirmed that the potential-energy (PE) surfaces of these two states will cross each other to form a conical intersection in the vicinity of the Franck–Condon (FC) region [13]. The studies have qualitatively indicated that the strong vibronic coupling may lead to an ultrafast nonadiabatic transition from the 1^2B_1 to 1^2A_2 state and drastically shorten the lifetime of the 1^2B_1 state, rendering the 1^2B_1 spectrum structureless. These findings provide us with a starting point for the investigation of the electronic structure of the pyrrolyl radical.

The goal of the present paper is a quantitative simulation of the photodetachment spectrum of the pyrrolide anion in order to improve the understanding of the different structure of these two bands. Multireference electronic structure calculations are performed to identify the relevant vibrational modes associated with this conical intersection. The electron-vibration coupling parameters are derived by a least-squares fitting procedure. The basic features of the 1^2A_2 and 1^2B_1 bands will be analyzed by the calculation of vibronic spectra within a time-independent framework.

2. Theoretical framework

2.1. Photodetachment

Photodetachment is the detachment of an electron from an *anion* by electromagnetic radiation. Our intention is to investigate the photodetachment from the pyrrolide anion, i.e., the photoelectric effect for $C_4H_4N^-$ ($\hbar = 1$ throughout):

$$C_4H_4N^- + \omega_0 \rightarrow C_4H_4N + e^- + E_k. \tag{2.1}$$

ω_0 denotes the photon energy and E_k the kinetic energy of the photoelectron e^-. The energy conservation law yields the electron binding energy $E = \omega_0 - E_k$. The threshold for photodetachment is the electron affinity EA, i.e., the difference of the ground state energy of the pyrrolyl radical, C_4H_4N, and the ground state energy of $C_4H_4N^-$. Thus the total energy range is

$$EA \leqslant E \leqslant \omega_0. \tag{2.2}$$

For $\omega_0 = 3.408$ eV (corresponding to the wavelength $\lambda_0 = 363.8$ nm of the exciting laser used in the experiment [13]), detachment from the 1^1A_1 ground state of pyrrolide can lead to the 1^2A_2 ground state and the 1^2B_1 first excited state of pyrrolyl. Detachment leading to the 1^2A_1 second excited state is not possible with this photon energy.

2.2. Hamiltonian

The vibronic coupling physics is treated in the diabatic electronic basis $\{\Phi_n(\mathbf{r},\mathbf{Q})\}_{n=1,2}$ since this greatly simplifies the numerical calculations compared to a treatment in the adiabatic picture. Here $\mathbf{r}$ denotes collectively the electronic coordinates and $\mathbf{Q}$ the set of vibrational normal coordinates. Φ_1 corresponds to the 1^2A_2 ground state and Φ_2 to the 1^2B_1 first excited state of the pyrrolyl radical. Expanding $\langle\Phi_n(\mathbf{Q})|\widehat{H}_{el}(\mathbf{Q})|\Phi_m(\mathbf{Q})\rangle - V_0(\mathbf{Q})\delta_{nm}$ ($\widehat{H}_{el}$ being the electronic Hamiltonian) about $\mathbf{Q} = 0$ up to first order leads to the approximate two-state multimode matrix Hamiltonian of linear vibronic coupling theory [14]:

$$\widehat{\mathbf{H}} = (\widehat{T}_N + V_0(\mathbf{Q}))\mathbf{1}_2 + \begin{pmatrix} E_1 + \sum_t \kappa_t^{(1)} Q_t & \sum_c \lambda_c Q_c \\ \sum_c \lambda_c Q_c & E_2 + \sum_t \kappa_t^{(2)} Q_t \end{pmatrix}, \tag{2.3}$$

where

$$\widehat{T}_N = -\frac{1}{2}\sum_t \omega_t \frac{\partial^2}{\partial Q_t^2} - \frac{1}{2}\sum_c \omega_c \frac{\partial^2}{\partial Q_c^2} \tag{2.4}$$

is the nuclear kinetic energy operator and

$$V_0(\mathbf{Q}) = \frac{1}{2}\sum_t \omega_t Q_t^2 + \frac{1}{2}\sum_c \omega_c Q_c^2 \tag{2.5}$$

the nuclear ground state potential of the pyrrolide anion in the harmonic approximation. Q_i denotes the dimensionless normal coordinate and ω_i the harmonic frequency of the ith vibrational mode. E_n are the vertical detachment energies, $\kappa_t^{(n)}$ the first order *intrastate* and λ_c the first order 1^2B_1–1^2A_2 *interstate* electron-vibrational coupling constants. Due to symmetry considerations (see Section 2.3), the sums run only over either a set of coupling modes or a set of tuning modes, indicated by "c" and "t", respectively. Coupling modes ν_c are those modes that couple