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On the Jahn–Teller and pseudo-Jahn–Teller effects in the photoelectron spectrum of cyclopropane

T.S. Venkatesan [a], S. Mahapatra [a,*], H. Köppel [b], L.S. Cederbaum [b]

[a] School of Chemistry, University of Hyderabad, Hyderabad 500 046, India
[b] Theoretical Chemistry, Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany

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Abstract

We present a theoretical account of the Jahn–Teller (JT) and pseudo-Jahn–Teller (PJT) effects in the photoelectron spectrum of cyclopropane. The PJT interactions between the two JT split $\tilde{X}^2E'$ and $\tilde{A}^2E''$ electronic states of the cyclopropane radical cation are examined. Nuclear dynamical simulations on the resulting four coupled electronic states including fourteen relevant vibrational modes are carried out by a wave packet propagation approach employing the multiconfiguration time-dependent Hartree algorithm. The theoretical results are compared with recent experimental photoelectron spectroscopic data.

Keywords: Jahn–Teller and pseudo-Jahn–Teller effects; Conical intersections; Nonadiabatic coupling

1. Introduction

The Jahn–Teller (JT) effect [1,2] – that a highly symmetric nonlinear molecule in degenerate electronic state tends to distort to a configuration of reduced symmetry – is one of the most important phenomena in chemistry [3–6]. The immediate consequence of JT interactions is the occurrence of *conical intersections* [7–9] of electronic potential energy surfaces (PESs). In this situation the nuclear motion ceases to be confined to a single PES and the adiabatic or Born–Oppenheimer (BO) approximation [10] breaks down. In more general terms, a nonadiabatic situation arises and as a result electronic transitions take place during nuclear vibrations [7]. This often leads to highly complex nuclear dynamics, a simulation of which requires to go beyond the BO description [7,9,11]. In such a situation, it is necessary to resort to a diabatic electronic representation [12] in order to avoid the diverging nature of the nonadiabatic coupling elements of the adiabatic electronic representation. Another class of interaction between a degenerate and a nondegenerate or two degenerate electronic states is also possible and is known as pseudo-Jahn–Teller (PJT) type of interaction [6,7,9,13–15].

In the present article, we focus on the photoionization spectroscopy of cyclopropane (CP) which represents a paradigm of simultaneous JT and PJT effects. Ionization of an electron from the $3e'$ and $1e''$ valence molecular orbitals of CP prepares the cyclopropane radical cation (CP^+) in its ground $\tilde{X}^2E'$ and first excited $\tilde{A}^2E''$ electronic states, respectively. At the undistorted equilibrium configuration, both CP and CP^+ belong to the D_{3h} molecular point group. The 21 vibrational degrees of freedom of CP are grouped into $3a_1'$, a_2', $4e'$, a_1'', $2a_2''$, and $3e''$ irreducible representations of the D_{3h} point group. Elementary symmetry selection rule suggests that the degeneracy of both the $\tilde{X}$ and $\tilde{A}$ electronic states of CP^+ would split in first order upon distortion along the degenerate e' vibrational modes. The components of the two JT split electronic states may also exhibit PJT type of interactions through the e'', a_1'', and a_2'' vibrational modes [16]. The photoelectron spectrum of CP was recorded by different experimental groups [17–25]. The experimental results revealed a bimodal intensity distribu-

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[*] Corresponding author. Tel.: +91 40 23011537; fax: +91 40 23012460.
E-mail addresses: smsc@uohyd.ernet.in (S. Mahapatra), Horst.Koeppel@pci.uni-heidelberg.de (H. Köppel).

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tion of the first and a highly diffuse structure of the second photoelectron bands.

We recently carried out detailed electronic structure calculations in order to construct the electronic PESs (and their coupling surfaces) of CP^+ along its 21 vibrational degrees of freedom [16,26]. The equilibrium geometry of CP in its electronic ground state ($\tilde{X}^1A_1'$) was optimized at the MP2 level of theory using the cc-pVTZ basis set of Dunning [27], and the dimensionless normal coordinates were calculated from the MP2 force field. The adiabatic PESs of the cationic electronic states along the dimensionless normal coordinates of each of the 21 vibrational modes were derived from the vertical ionization energies calculated by the outer valence Green's function (OVGF) method [28,29]. These potential energies along each vibrational mode have been fitted in order to calculate the parameters necessary to formulate a vibronic coupling model [16,26].

In a previous article, we examined the multimode JT effect in the $\tilde{X}^2E'$ electronic manifold of CP^+ devising a quadratic vibronic coupling scheme [16]. The theoretical results revealed a bimodal distribution of spectral intensity [16] in good accord with the experimental results [25]. The calculated splitting of ~0.80 eV between the two maxima of the bimodal spectral profile compares well with the experimental value of ~0.78 eV [25]. Two Condon active (a_1') and three JT active (e') vibrational modes were found to contribute mostly to the nuclear dynamics in this electronic manifold. In addition, it was found that the progressions in the low-energy wing of the envelope are mainly formed by the JT active v_4 (CH_2 wagging) and v_5 (ring deformation) vibrational modes. The average spacing between the successive peaks was found to be in agreement with the experimental value of ~60 meV [25]. However, in contrast to the experimental results, highly irregular vibronic structures in the low-energy wing of the theoretical spectrum was found. Also, the second maximum of the bimodal spectral profile revealed more structures than that observed in the experimental envelope [16].

The second photoelectron band of CP^+, attributed to the vibronic structure of $\tilde{A}^2E''$ electronic manifold, is highly diffuse and broad [25]. In order to reveal the coupling effects of various vibrational modes on the vibronic fine structure of this band, we first examined the nuclear dynamics employing a quadratic coupling scheme in the $\tilde{A}^2E''$ electronic manifold [26]. Dominant excitation of the v_2, v_3, v_4 and v_6 vibrational modes was found in the photoelectron band [26]. However, we note that the JT activity of the e' vibrational modes is relatively weak in the $\tilde{A}^2E''$ electronic manifold when compared to the same in the $\tilde{X}^2E'$ electronic manifold. Although the quadratic vibronic coupling results compare well with the experimental data, still, the theoretical envelope does not reveal the observed structureless and diffuse nature of the band.

The discussed discrepancies between the theoretical and experimental results motivated us to further examine the possible role of PJT interactions between the $\tilde{X}^2E'$ and $\tilde{A}^2E''$ electronic states of CP^+ and the intermode bilinear JT coupling terms. We found that only the a_1'' and one of the three e'' vibrational modes (both of CH_2 twisting type) are PJT active. Low-lying crossings of the $\tilde{X}$–$\tilde{A}$ states occurring in the energy range of the photoelectron bands have been discovered [26]. Therefore, we now here develop an extended diabatic vibronic Hamiltonian considering the intermode coupling terms, apart from the possible PJT interactions between the $\tilde{X}^2E'$ and $\tilde{A}^2E''$ electronic states of CP^+. The theoretical findings establish the importance of both the bilinear and the PJT couplings in the nuclear dynamics.

The simulation of the nuclear dynamics in the coupled $\tilde{X}^2E'$–$\tilde{A}^2E''$ electronic states is highly involved since it requires consideration of four interacting electronic states of CP^+ and fourteen relevant vibrational degrees of freedom. Such a task is computationally impossible with the matrix diagonalization approach and is therefore carried out by a wave packet (WP) propagation approach using the multiconfiguration time-dependent Hartree (MCTDH) scheme [30–32]. The theoretical methodology to treat the nuclear dynamics is briefly outlined in Section 2 and the results are presented and discussed in Section 3. The main findings of the paper are summarized in Section 4.

2. Theoretical methodology

The vibronic Hamiltonian used for the quantum WP dynamical simulations here comprises two low-lying degenerate $\tilde{X}^2E'$ and $\tilde{A}^2E''$ electronic states of CP^+ and 14 vibrational degrees of freedom. The latter are selected from the set of 21 vibrational degrees of freedom of CP^+ by analyzing their coupling strengths extracted from our extensive electronic structure data [16,26]. The Hamiltonian is constructed in terms of the dimensionless normal displacement coordinates (Q_i) of the electronic ground state of CP ($\tilde{X}^1A_1'$). The vibrational motion in the latter is treated as harmonic. In the following, we refer to Q_i as the dimensionless normal coordinate of the vibrational mode v_i with a harmonic vibrational frequency ω_i. Following the well known vibronic coupling theory [7], we represent the diabatic vibronic Hamiltonian of the coupled manifold of four interacting electronic states as

$$\mathscr{H} = \mathscr{H}_0\mathbf{1}_4 + \begin{pmatrix} \mathscr{W}_{11} & \mathscr{W}_{12} & \mathscr{W}_{13} & \mathscr{W}_{14} \\ & \mathscr{W}_{22} & \mathscr{W}_{23} & \mathscr{W}_{24} \\ \text{h.c.} & & \mathscr{W}_{33} & \mathscr{W}_{34} \\ & & & \mathscr{W}_{44} \end{pmatrix}, \tag{1}$$

where $\mathscr{H}_0$ is the Hamiltonian matrix associated with the electronic ground state of CP and is defined in terms of unperturbed harmonic oscillators with frequencies ω_i. The matrix Hamiltonian with elements $\mathscr{W}_{ij}$ in Eq. (1) describes the change in electronic energy upon ionization from the electronic ground state of CP. The elements $\mathscr{W}_{11}$ and $\mathscr{W}_{22}$ represent the two diabatic components of the $\tilde{X}^2E'$ electronic manifold and $\mathscr{W}_{12}$ is the coupling between them. $\mathscr{W}_{33}$ and $\mathscr{W}_{44}$ are the two diabatic components