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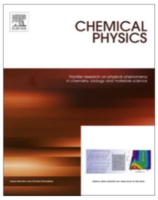

Radical cation spectroscopy of substituted alkyl phenyl ketones via tunnel ionization

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ABSTRACT

Mass spectra are measured for 2′-, 3′- and 4′-(*ortho*, *meta* and *para*) methyl substituted alkyl phenyl ketones excited at wavelengths ranging from 1200 to 1500 nm in the strong field regime. The selective loss of a methyl group from the acetyl group of the parent molecular ion upon excitation at ~1370 nm is attributed to an electronic resonance between ground D_0 and excited D_2 state of the radical cation. Depletion of the parent molecular ion is enhanced as the methyl substituent is moved from the 2′ to 3′ to 4′ position on the phenyl ring with respect to the acetyl group. The phenyl-acetyl dihedral angle is the relevant coordinate enabling excitation to the dissociative D_2 state. Calculations on the radical cation of 2′-methylacetophenone show two stable geometries with dihedral angles of 7 degrees and 63 degrees between the phenyl and acetyl groups. The barrier to rotation for the 2′ isomer limits population transfer to the D_2 state. In contrast, calculations on the radical cations of 3′- and 4′-methylacetophenone reveal no rotational barrier to prevent population transfer to the excited state, which is consistent with the enhanced dissociation yield in comparison with the 2′ substitution. The enhanced dissociation of the 4′ isomer as compared to the 3′ isomer is attributed to its lower moment of inertia about the dihedral angle.

1. Introduction

An emerging theme in the area of controlling chemical reactions in the strong field regime is the role of radical cation excited states in the dynamics of molecular dissociation [1,2]. When a molecule interacts with a strong field laser pulse ($>10^{13}$ W cm^{-2}), the radical cation can be produced via multiphoton and/or tunnel ionization [3–7], populating one or more electronic states. To distinguish tunnel from multiphoton ionization, the Keldysh parameter γ may be utilized [8,9]. This parameter is defined as the ratio of the laser frequency ω_o to a characteristic tunneling frequency ω_t

$$\gamma = \frac{\omega_o}{\omega_t} = \frac{\omega_o\sqrt{2\mathrm{IP}m_e}}{eE_o} \tag{1}$$

where IP is the ionization potential, E_0 is the laser field magnitude, m_e is the electron mass and e is the electron charge. If $\gamma \gg 1$, multiphoton ionization is the dominant mechanism, while tunnel ionization dominates if $\gamma \ll 1$, as illustrated in Fig. 1. Multiphoton ionization in the strong field regime typically populates a number of cation electronic states $|e_0\rangle, |e_1\rangle, |e_2\rangle, \ldots$ due to ladder climbing [10]. These states can relax through internal conversion to produce vibrationally hot molecules that can undergo a high degree of fragmentation. Although lowering the intensity of the excitation pulse that initiates multiphoton ionization can help minimize ladder climbing, this also decreases the observed ion signal. In the adiabatic limit, tunnel ionization leaves the molecule in its ground radical cation state $|e_0\rangle$ with little excess vibrational energy.

The contrast between molecular fragmentation patterns upon multiphoton and tunnel ionization was first demonstrated in linear polyenes [7], where excitation at 800 nm resulted in a high degree of fragmentation, while excitation at 1450 nm produced primarily singly and doubly charged parent molecular ion. The fragmentation at shorter wavelengths was explained in terms of non-adiabatic multi-electron dynamics. Reduced molecular fragmentation upon excitation with near-IR wavelengths as compared to 800 nm has since been observed in other molecules including naphthalene

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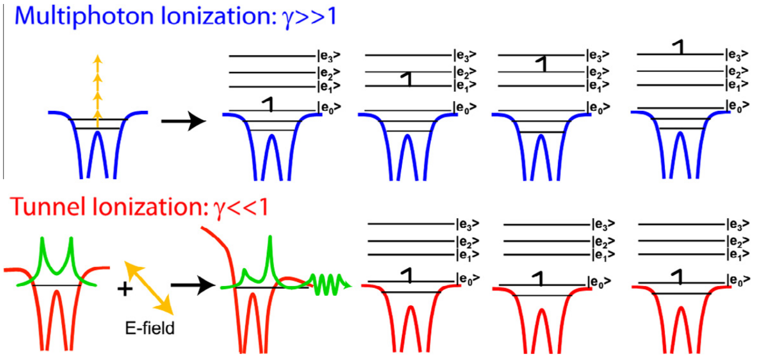

Fig. 1. A depiction of the distribution of electronic states in a molecule after multiphoton ionization (MPI) and tunnel ionization.

[11], anthracene [12], alkylphenols [13] and acetophenone [14]. We propose that the adiabatic ionization mechanism at longer wavelengths has important consequences for electronic spectroscopy and coherent control, as the "cold" parent molecular ion formed by tunnel ionization can be used as a "launch state" for further excitation [15].

Upon formation of a radical cation, excitation to higher lying electronic states can result in dissociation. Cationic resonances observed via photoelectron spectroscopy have been shown to correlate with strong field fragmentation patterns in Ni(CO)$_4^+$ and Fe(CO)$_5^+$, where enhanced fragmentation was observed upon excitation with the resonant wavelengths of 1350 nm for Ni(CO)$_4^+$ and 800 nm for Fe(CO)$_5^+$ [16]. Enhanced fragmentation of cycloketones upon excitation with 394 nm as compared to 788 nm was attributed to features in their respective radical cation photoabsorption spectra [17,18]. Similar dissociation was observed for large aromatic molecules excited with 1400 nm [12]. Mass-resolved, strong field excitation using laser pulses ranging from 1200 to 1500 nm has revealed the existence of a cationic resonance at 1370 nm in alkyl phenyl ketones. The resonance is supported by calculations of the cationic ground and excited state energies [1]. Calculations show the existence of radical cationic states and reveal their role in fragmentation mechanisms [1,19–22]. Transient cationic resonances have also been observed in pump–probe studies on halomethanes [23,24] and azobenzene [19].

We have recently reported that a cationic resonance in alkyl phenyl ketones upon excitation with ~0.9 eV (1370 nm) IR photons leads to selective formation of the benzoyl fragmentation product, supported by quantum calculations of the acetophenone and propiophenone radical cations [1]. Calculations show that the ground ionic surface D_0 and second ionic excited state D_2 are separated by 0.87 and 0.88 eV at the energetic minimum of the ground radical cation surface for acetophenone and propiophenone, respectively. The formation mechanism of the benzoyl fragment upon excitation from D_0 to D_2 is shown in Fig. 2. Upon vertical ionization, the radical cation of acetophenone is produced at a torsional angle of 0 degrees between the phenyl and acetyl moieties. Subsequent relaxation of the cation increases the phenyl-acetyl dihedral angle to 44 degrees, with the oscillator strength $f(D_0–D_2)$ between the two states increasing from zero upon vertical excitation to 0.046 at the relaxed geometry. Once the molecule reaches this geometry, the trailing edge of the laser pulse excites a resonant transition to the D_2 state. The wavepacket then propagates on the D_2 surface to a conical intersection of the D_0, D_1, and D_2 ionic surfaces at a torsional angle of zero degrees. The nonadiabatic nature of the conical intersection converts the electronic energy in the torsional coordinate to vibrational energy in the C—CH_3 bond length coordinate leading to bond dissociation.

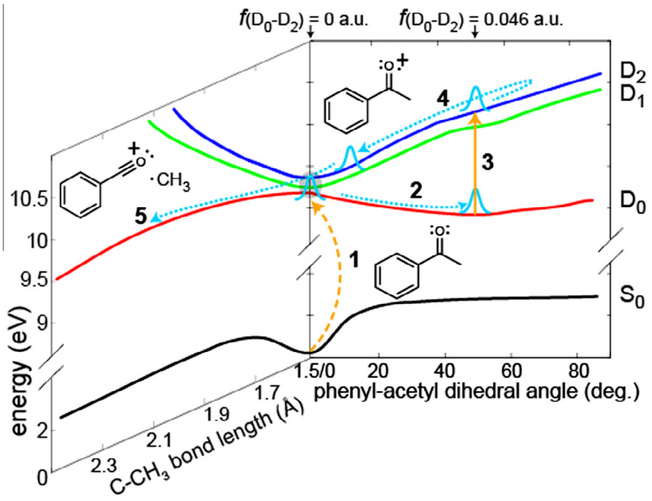

Fig. 2. The proposed mechanism for the dissociation of the acetophenone radical cation [1]. The black, red, green, and blue curves correspond to the S_0, D_0, D_1, and D_2 states respectively. Tunnel ionization (step 1) launches a torsional wavepacket on the ground state D_0 of the parent molecular ion, which relaxes to its equilibrium geometry (step 2). At the energy minimum, the wavepacket undergoes a one-photon resonant transition to the D_2 state (step 3). The wavepacket proceeds down the D_2 surface reaching a conical intersection (step 4) that converts electronic energy to vibrational energy leading to bond dissociation along the C—CH_3 bond coordinate (step 5). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

This work investigates fragmentation yields in the family of methyl substituted alkyl phenyl ketones, 2′-, 3′-, and 4′-methylacetophenone. Mass spectra are measured as a function of strong field excitation wavelength ranging from 1200 to 1500 nm. Calculations are performed on the molecules to determine the nuclear configurations corresponding to the energy minima of the neutral molecules and radical cations. The results are rationalized in terms of the energies and phenyl-acetyl dihedral angles in the respective optimized geometries of the radical cations of 2′-, 3′-, and 4′-methylacetophenone.

2. Experimental

The apparatus used to perform the measurements of the electronic structure of a radical cation has been described previously [1]. Briefly, a Ti:Sapphire amplifier producing 1 mJ, 50 fs pulses was used to pump an optical parametric amplifier (OPA) to generate tunable IR pulses from 1150 to 1550 nm with pulse durations from 50 to 100 fs. Pulse durations for the following experiments were maintained at 60 fs across the tuning range as measured by