Journal of Quantitative Spectroscopy & Radiative Transfer 173 (2016) 92–105

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Journal of
Quantitative
Spectroscopy &
Radiative
Transfer

Vibrational modes in excited Rydberg states of acetone: A computational study

Aparna Shastri*, Param Jeet Singh

Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

ARTICLE INFO

Article history:
Received 4 December 2015
Accepted 6 January 2016
Available online 14 January 2016

Keywords:
Rydberg states
TDDFT
Geometry optimization
Vibrational frequencies
Vibronic bands

ABSTRACT

Computational studies of electronically excited states of the acetone molecule [$(CH_3)_2CO$] and its fully deuterated isotopologue [$(CD_3)_2CO$] are performed using the time dependent density functional (TDDFT) methodology. In addition to vertical excitation energies for singlet and triplet states, equilibrium geometries and vibrational frequencies of the $n=3$ Rydberg states ($3s$, $3p$ and $3d$) are obtained. This is the first report of geometry optimization and frequency calculations for the $3p_x$, $3p_z$, $3d_{yz}$, $3d_{xy}$, $3d_{xz}$, $3d_{x2-y2}$ and $3d_{z2}$ Rydberg states. Results of the geometry optimization indicate that the molecule retains approximate C_{2V} geometry in most of these excited Rydberg states, with the most significant structural change seen in the CCO bond angle which is found to be reduced from the ground state value. Detailed comparison of the computationally predicted vibrational wavenumbers with experimental studies helps to confirm several of the earlier vibronic assignments while leading to revised/new assignments for some of the bands. The important role of hot bands in analysis of the room temperature photoabsorption spectra of acetone is corroborated by this study. While the vibrational frequencies in excited Rydberg states are overall found to be close to those of the ionic ground state, geometry optimization and vibrational frequency computation for each excited state proves to be very useful to arrive at a consistent set of vibronic assignments. Isotopic substitution helps in consolidating and confirming assignments. An offshoot of this study is the interpretation of the band at ~8.47 eV as the π–$3s$ Rydberg transition converging to the second ionization potential.

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1. Introduction

An important issue in interpretation of the electronic absorption spectra of molecules is the identification and assignment of the vibronic structure in terms of which specific vibrational modes are excited along with a given electronic transition. This is often a non trivial task as the geometries of molecules in excited states are in general different from the ground state, leading to variations in vibrational frequencies as well. For excited states of Rydberg nature, vibrational frequencies are generally expected to be close to those of the corresponding cationic state to which the series converges [1,2]. This approach has been found to give reasonably good results and has been used widely in analysis of vibronic spectra accompanying Rydberg transitions [3,4]. However, in some cases, due to differences in geometry between the neutral excited state and ionic ground state or perturbations like valence-Rydberg mixing, this assumption may not lead to accurate assignments. This is all the more so for low lying Rydberg states, where interaction of the Rydberg electron with the molecular core assumes greater importance.

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* Corresponding author. Tel.: +91 22 25590343; fax: +91 22 25502652.
E-mail address: ashastri@barc.gov.in (A. Shastri).

http://dx.doi.org/10.1016/j.jqsrt.2016.01.011
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Since it is typically the low lying Rydberg states which exhibit well resolved vibronic peaks in absorption spectra, it is of interest to ask the question 'To what extent is the assumption of Rydberg state frequencies being close to that of ionic ground state frequencies valid?' One possible way of shedding some light on this issue is to use quantum chemical computations to generate the equilibrium geometry and vibrational frequencies of the molecule in the electronically excited (Rydberg) states of interest and compare with the experimental spectra. The electronic absorption spectrum of acetone in the VUV region (6–10 eV) exhibits rich vibronic structure associated with the low lying Rydberg states and presents an interesting case study from this perspective. Acetone being the simplest aliphatic derivative of the carbonyl family is a prototype for understanding the spectroscopic properties of this family of compounds. Due to its importance in photobiology, interstellar and atmospheric photochemistry, electronically excited states of acetone have been and continue to be extensively studied, both experimentally [3–21] and theoretically [15,18,22–35].

Experimental studies of the Rydberg states of acetone include the very early reports of its absorption spectra [5–7] using conventional laboratory sources followed by more detailed photoabsorption studies [3,4,8,9,20] and several laser based multiphoton studies [10–19,21]. Recently, we have reported comprehensive VUV photoabsorption studies of acetone-h_6 and acetone-d_6 using synchrotron radiation [3,4]. Rydberg series of type ns, np_y, np_z, nd_{yz}, nd_{x2-y2} and nd_{xy} (dipole allowed) were assigned using a quantum defect analysis. Observed vibronic features were assigned to various modes, mainly based on theoretically predicted ionic frequencies [18] and a few experimental measurements reported by single photon absorption [8,9] as well as resonance enhanced multiphoton ionization (REMPI) techniques[10,13,15,18,36]. A comparison of the vibronic spectra of acetone-h_6 and acetone-d_6 helped in verifying and consolidating some of the assignments [3,4].

On the theoretical front, a variety of computational methods have been used to study the electronically excited states of acetone, mostly confined to the first few low lying valence states. These include early works using self consistent field (SCF) and configuration interaction (CI) calculations [35], to more sophisticated approaches like time dependent density functional theory (TDDFT) [32,34], equation of motion-coupled-cluster with single and double excitations (EOM-CCSD) [26,37], complete active space self consistent field (CASSCF) [26,32], multi-configuration approach combined with second order perturbation (CASPT2) [26], etc. Recently, using the molecular quantum defect method (MQDO), Lavin and Velasco [22] have predicted excited state energies and oscillator strengths for the ns and nd Rydberg states up to $n=10$. Geometry optimization and vibrational frequency computations in the first few singlet and triplet valence states of acetone using single state CASSCF [29] and quantum Monte Carlo [23] methods have been reported, however comparison of the results with experiment is lacking as vibronic bands in these valence states have not been observed so far. The TDDFT and CASSCF/CASMP2 methods have been used to investigate the potential energy surfaces of the first few excited states by Diau et al. [32], who have carried out state specific studies to obtain equilibrium structures and vibrational frequencies of three valence and two Rydberg states ($3s$ and $3p_y$). Comparison with experimental values was limited to the then available data and a few discrepancies like the surprisingly high value of the CO out of plane bend (1275 cm^{-1}) compared to the ground state value (484 cm^{-1}) were seen, warranting further investigations of these states. In addition to these works, there have been a number of recent papers probing the photodissociation dynamics of acetone via the first excited valence state ($^{1,3}n–\pi^*$) [24,28] in order to understand the mechanism of Norrish type I reactions or α-CC bond cleavage.

To the best of our knowledge, there is no report on geometry optimization of higher excited states, in particular the Rydberg states $3p_x$, $3p_z$, $3d_{yz}$, $3d_{xy}$, $3d_{xz}$, $3d_{x2-y2}$ and $3d_{z2}$. The relative scarcity of computational studies of excited state geometries and vibrational frequencies could be partly due to the fact that ab initio methods for such computations are very expensive and time consuming. While the ab initio methods are undoubtedly superior when it comes to a balanced and accurate description of ground and excited states, the TDDFT method offers the advantage of being relatively inexpensive, fast and simple to implement. Although TDDFT is known to have some issues for description of Rydberg states, the results are expected to be fairly accurate for low lying Rydberg states [25,38–43]. In this paper we report on geometry optimization and vibrational frequency computations of the $3s$, $3p$ and $3d$ Rydberg states of acetone-h_6 (-d_6) using TDDFT and compare the results with the experimentally observed vibrational frequencies in these states. The main aim of the present work is to evaluate the extent to which the similarity in Rydberg states and ionic ground states is obeyed in acetone while presenting a consolidated set of TDDFT based computational results for the excited Rydberg states of acetone-h_6 (-d_6).

2. Computational methods

Quantum chemical computations are carried out using the DFT and TDDFT formalisms for ground state and excited states respectively using the GAMESS(US) code [44] on a LINUX based cluster platform. Initially, geometry optimization of the neutral ground state and the cationic ground state of the molecule are performed using DFT. The molecular coordinates are chosen such that the CCCO group is in the XZ plane which specifies the classification of the b_1 and b_2 vibrational symmetry mode symmetries [4]. Vertical excitation energies for singlet and triplet states are computed keeping the molecular geometry fixed at the ground state optimized structure. Computations are performed using the hybrid exchange correlation functionals Becke-3–Lee–Yang–Parr (B3LYP) [45,46] as well as the Coulomb attenuating method-B3LYP (CAM-B3LYP) [47]. Basis sets used are the Pople's split valence basis set 6–31G [48,49] with polarization and diffuse functions added. Although the CAM-B3LYP functional has been reported to give a good performance for excitation

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