Journal of Quantitative Spectroscopy & Radiative Transfer 114 (2013) 20–28

Contents lists available at SciVerse ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

# Effect of isotopic substitution in the electronic absorption spectrum of acetone: VUV photoabsorption studies of acetone-$d_6$

Param Jeet Singh, Aparna Shastri *, B.N. Raja Sekhar, R. D'Souza, B.N. Jagatap

*Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*

ARTICLE INFO

*Article history:*
Received 20 June 2012
Received in revised form
17 August 2012
Accepted 17 August 2012
Available online 25 August 2012

*Keywords:*
Acetone-$d_6$
Vacuum ultraviolet
Photoabsorption
Synchrotron radiation
Vibronic assignments
Electronic spectrum

ABSTRACT

The VUV photoabsorption spectrum of acetone-$d_6$ is recorded in the energy region 6–10 eV using synchrotron radiation at a resolving power of ~1000. Extensive Rydberg series are observed converging to its first ionization limit (9.708 eV). Quantum defect analysis and vibronic analysis of higher Rydberg series members have been reported for the first time. A comparative study of the Rydberg series and accompanying vibronic structure observed in acetone-$h_6$ and acetone-$d_6$ has clarified and consolidated many of the vibronic assignments. The frequency of the $\nu_{19}'$ mode (CO in-plane bend) of the $3p_y$ state is obtained as $340 \pm 5$ cm$^{-1}$ on the basis of observation of an extensive progression of this mode.

## 1. Introduction

The importance of acetone in photochemistry and interstellar chemistry and its benchmark status in the study of methyl torsional effects have stimulated a large number of investigations over the past few decades [1–25]. The electronic absorption spectrum of acetone has been extensively studied in the region of the 3s and 3p Rydberg states [1,13–22], whereas studies of the 3d states and higher Rydberg series members are relatively sparse [1,7,13]. An interesting feature of the acetone absorption spectrum is that all observed transitions in the VUV region are of Rydberg type, with valence states making an indirect appearance through vibronic coupling with the Rydberg states [13,15]. Recently, we have reported a comprehensive VUV photoabsorption study of acetone-$h_6$ using synchrotron radiation [1]. As discussed there, the $\nu_{12}$ ($a_2$) and $\nu_{24}$ ($b_1$) torsional modes of acetone-$h_6$ play a very important role in its room temperature absorption spectrum. The low frequency (77.8 and 124.5 cm$^{-1}$) of these modes gives rise to considerable hot band structure in the electronic absorption spectrum [1]. By appropriate consideration of symmetry based selection rules for vibronic transitions and the role of hot bands in the room temperature absorption spectrum, several discrepancies in earlier work [7] were clarified and a more complete analysis was presented. Nevertheless, there are still some open issues like transitions with multiple assignments, unambiguous location of the $\nu_{00}$ origins in some of the Rydberg states and anomalous quantum defects observed in the $nd_{xy}$ series [1].

Isotopic substitution is a well-known tool for confirming vibrational assignments in molecular spectra [26]. In particular, frequency shifts expected for various normal modes can be used to ascertain the accuracy of the assignments. This technique has been effectively used in VUV photoabsorption studies reported recently [27–31]. Several earlier papers on the excited electronic states of acetone have also used the isotope shift to assign vibrational features in 3s and 3p states [13,15–23]. The only

---

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

0022-4073/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jqsrt.2012.08.022

prior study of deuteroacetone which covers the entire VUV region (6.2–9.7 eV) is the early report by Lawson and Duncan [23] using a hydrogen discharge source and photographic plate detection. Subsequent reports [13,15–22] have carried out more detailed studies in particular and important wavelength regions. The objective of the present work is to consolidate the Rydberg series analysis and vibronic assignments in the entire VUV region up to the first ionization limit by a comparative study of the electronic absorption spectrum of $(CH_3)_2CO$ with its deuterated isotopomer $(CD_3)_2CO$. The difficulty in making vibrational assignments in excited electronic state is that direct measurements of vibrational frequencies are not usually available, and one has to depend on theoretically predicted values or ionic frequencies. Since the geometry of the excited states could be considerably different from the ground state or ionic geometries, there is always some element of uncertainty in assignments carried out using these values. A comparison of the VUV photoabsorption spectra of acetone-$d_6$ and acetone-$h_6$ serves to clarify some of these ambiguities and gives new insights into the excited state electronic structure. In the deuterated compound, the vibrations involving the $CH_3$ groups are expected to shift considerably towards lower frequencies whereas relatively smaller shifts are expected for normal modes that do not involve the H atoms. It may be noted that the frequencies of the torsional modes in acetone-$d_6$ are lower (53.4 and 96 $cm^{-1}$) than in acetone-$h_6$ and hence the relative populations with respect to the ground state are expected to be greater in acetone-$d_6$ ( ~77% and 62% ) as compared to acetone-$h_6$ ( ~70% and 55%). Consequently, similar to the room temperature absorption spectrum of acetone-$h_6$ [1], the spectrum of acetone-$d_6$ is also expected to exhibit substantial contribution from hot bands due to the torsional modes. The current study addresses these issues and to the best of our knowledge is the first detailed VUV photoabsorption study of acetone-$d_6$ up to its first ionization limit.

## 2. Experimental

VUV absorption experiments are performed at the Photophysics beamline at the synchrotron radiation facility Indus-1. Details of the beamline and experimental setup have been discussed in earlier publications [1 and references there in]. Briefly, a 1-meter Seya-Namioka monochromator is used to disperse the synchrotron radiation which is made to pass through a 25 cm length stainless steel absorption cell with LiF windows. The resolving power of the monochromator is $\sim 10^3$ which results in a resolution better than 45 $cm^{-1}$ in the VUV region. The sample is held in a glass vial and connected to the absorption cell through a gas introduction system consisting of several Swagelok valves and adapters. Acetone-$d_6$ of stated purity 99.9% procured from Aldrich, USA, is used after subjecting it to a few freeze–pump–thaw cycles to eliminate volatile impurities. The detection system consists of a sodium salicylate coated quartz window coupled to a UV-visible photomultiplier. The recorded signal is normalized at every step with respect to the synchrotron beam current. The transmitted intensity through the evacuated cell (base pressure $\sim 1 \times 10^{-6}$ mbar) serves as the reference or $I_0$ whereas the transmitted intensity through the sample filled in the cell is $I$. The absorption spectrum is generated using the Beer–Lambert law by plotting $\ln(I_0/I)$ as a function of wavelength at a step size of 0.5 Å. Absorption spectra are recorded at several sample pressures of $10^{-4}$ mbar to 1 mbar. Atomic absorption lines of Xenon are used as wavelength standards for calibration of the spectrum.

## 3. Results and discussions

The VUV photoabsorption spectrum of acetone-$d_6$ recorded using synchrotron radiation is shown in Fig. 1 in energy and wavenumber scale. The dotted curve represents the VUV photoabsorption spectrum of acetone-$h_6$. Transitions observed in the VUV region are all of Rydberg type, with several transitions being accompanied by extensive vibrational structure. The spectral analysis may be accordingly divided into two parts, viz. the quantum defect analysis of the Rydberg series and the vibronic analysis of the accompanying vibrational structure (Fig. 2).

### 3.1. Rydberg series analysis

In the energy region 6.0–10.0 eV extensive Rydberg series converging to the lowest ionization limit of acetone-$d_6$ (9.708 eV) are observed (c.f. Fig. 1). Each series can be fitted to the well-known Rydberg formula: $E_n = IP - R/(n-\delta_l)^2$where $E_n$ is the energy of the transition, $IP$ is the ionization potential, $R$ is the Rydberg constant, $n$ is the principal quantum number and $\delta_l$ is the quantum defect, which depends on the angular momentum $l$. The quantum defect analysis and vibronic analysis of the Rydberg series ns, $np_x$, $np_y$, $np_z$, $nd_{xy}$, $nd_{yz}$ and $nd_{x^2-y^2}$ observed for acetone-$h_6$ have been summarized in a recent publication [1]. From molecular beam photoionization studies of acetone-$h_6$ and acetone-$d_6$, the experimentally measured first ionization potential of acetone-$d_6$ is same as that of acetone-$h_6$ [32]. Rydberg series corresponding to the ns, np and nd type are identified for acetone-$d_6$ assuming the same value for ionization potential used earlier [1]. The observed Rydberg transitions of acetone-$d_6$ have been classified based on a quantum defect analysis and are tabulated in Table 1, along with the Rydberg series of acetone-$h_6$ (lower entries) for comparison. As seen from Table 1, the highest principal quantum number observed is $n=10$ for ns and $nd_{yz}$. For $np_y$ and $np_z$, the series are traced up to $n=8$, whereas in $nd_{x^2-y^2}$ and $nd_{xy}$, the maximum n observed is 7 and 9 respectively. In the $nd_{xy}$ series, a few members ($n=5,7,8$) are not observed clearly, possibly due to merging with more intense features. The various Rydberg series are characterized by average quantum defects of 0.97 (ns), 0.52 ($np_y$ and $np_z$), 0.35 ($nd_{yz}$), 0.13 ($nd_{x^2-y^2}$) and 0.03 ($nd_{xy}$). The $nd_{yz}$ series, which could not be distinguished beyond $n=7$ in acetone-$h_6$ [1], is extended up to $n=10$ in acetone-$d_6$. Quantum defects for acetone and deuteroacetone are almost equal for series with a given orbital angular momentum, as expected, except for some minor