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Theoretical study on intensities in the discrete and continuum electronic spectrum of acetone

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ABSTRACT

Intensities, expressed as oscillator strengths for the discrete and, as cross-sections for the continuum electronic spectrum of acetone are reported. The calculations have been performed with the molecular quantum defect method (MQDO), which has proved to be a very adequate tool for this type of studies in other organic molecules. The present work covers transitions to more highly excited Rydberg states than had previously been reported. The quality of the oscillator strengths has been assessed by comparison with scarce data available in the literature, and by its compliance with the expected trends along the Rydberg series. Electronic partial photoionization cross-sections for acetone over the 10–50 eV photon energy are also calculated. Cross-section profiles for Rydberg series that constitute the ionization channels of acetone from the outermost orbital in its ground state are reported for the first time.

1. Introduction

In the last decades, a great deal of work has been devoted to the calculation of molecular electronic spectra, not only by their practical importance in fields such as astrophysics, atmospheric chemistry, astrobiology, etc., but also by the fact that they provide a good indicator of the reliability of approximate theoretical procedures. In the discrete region, molecular electronic spectra are characterized by the excitation energies and the band intensities. The former have been object of several theoretical and experimental investigations, and, for a number of molecules, very accurate values are available. Significantly less work has been done in determining oscillator strengths, or *f*-values, that are the magnitudes commonly used to discuss intensities in the discrete absorption spectrum. This imbalance is mainly due to the complexity of both experimental and theoretical approaches to determine *f*-values, as has been stressed in a recent study on oscillator strengths for electronic transitions in molecules [1]. On the other hand, the quantitative description of the continuum region of spectrum requires ionization potential as well as intensities data. The energies of parent ionic states have been studied greatly in many molecules whereas relatively little information is available on intensities of photoelectron spectra (given by the so-called electronic partial cross-sections [2]), despite synchrotron radiation and electron impact sources having provided energy necessary to produce excitations over wide spectral ranges. There have only been a few investigations of the intensity of the ionization continuum because of the difficulty of obtaining accurate continuum electronic wave functions.

The acetone molecule, $(CH_3)_2CO$, illustrates the above mentioned situation. Since Noyes et al. [3] photographed for the first time the ultraviolet absorption spectrum of acetone vapor, most of the studies have mainly focused on the location and assignments of the electronically excited states of this molecule. It is now well known that, below the first ionization potential, the vacuum-ultraviolet (VUV) absorption spectrum of $(CH_3)_2CO$ shows a rich Rydberg structure

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together with some valence states. The most complete assignment of the Rydberg structure of acetone has been proposed, to our knowledge, by Nobre et al. [4] who, using high resolution VUV photoabsorption spectroscopy, were able to identify the *n*s, *n*p and *n*d Rydberg series up to very high values of *n*. By contrast, measurements of oscillator strengths for Rydberg transitions are extremely scarce; in fact, as far as we know, *f*-values have been reported [5–8] only for the transition from the ground state to the lowest Rydberg state, the 3s $^1B_2$ state. Previous theoretical calculations using extensive *ab initio* and time-dependent density functional theory (TDDFT) calculations on acetone have been performed by several authors [9–11,1]. In these works, values of oscillator strengths were only supplied for transitions to the lower members ($n=3$, 4) of the Rydberg series. Moreover, considerable discrepancies among them have been observed. Concerning the photoionization cross-sections, measurements have been focused on the near-threshold region [12–14].

This study has been prompted by the scarcity of intensity data in both discrete and continuum spectra of acetone needed for a better insight into the spectral features of this molecule. Hence, in this paper, we report theoretical oscillator strengths for dipole-allowed transitions to Rydberg states in $(CH_3)_2CO$ that have not been, to our knowledge, previously studied either through measurements or calculations. In addition, the cross-sections for the photoionization channels leading to the ground state of the molecular ion, $(CH_3)_2CO^+$ have been investigated up to a photon energy of 50 eV. The calculations have been carried out with the molecular quantum defect orbital (MQDO) method [15]. This approach has supplied reliable intensities for Rydberg transitions in recent applications to three other carbonyl compounds [16–18]. The MQDO method has also been shown to produce accurate photoionization cross-sections in different molecular systems (see Ref. [19] and references therein).

In addition to their potential fundamental importance, data reported here can be relevant in atmospheric chemistry, astrophysics, and combustion chemistry. Acetone is an abundant and ubiquitous species in the terrestrial atmosphere [20] and its photolysis in the upper troposphere is believed to be an important source of HO_x, peroxy and alkoxy radicals [21,22] which can have an impact in atmospheric chemistry. Quantitative spectroscopic data, such as electronic transition probability are essential for the understanding of dissociation processes of $(CH_3)_2CO$, where Rydberg states are directly involved, in the atmosphere. Intensity data are also required to model the role that acetone plays in the interstellar medium where it has been detected [23,24]. In combustion studies, photoionization cross-section data of $(CH_3)_2CO$, among other species, are necessary in order to obtain concentrations of flame species combustion [13,25].

2. Method of calculation

The absorption oscillator strength for a transition between two states *i* and *j* is defined as

$$f_{ij}=\frac{2}{3}\Delta E|M_{ij}|^2, \tag{1}$$

where ΔE is the transition energy in hartrees and M_{ij} is the transition matrix element between the initial and final state wave functions, Ψ_i and Ψ_j, respectively. In the electric dipole approximation,

$$M_{ij}=\langle\Psi_i|r|\Psi_j\rangle \tag{2}$$

The photoionization cross-section is expressed in units of megabarns (Mb), as follows [26]

$$\sigma=2.6891\left(\frac{T+k^2}{g_i}\right)|M_{ij}|^2, \tag{3}$$

where T is the ionization potential in Rydberg units of the initially bound electron, k^2 is the kinetic energy of the free electron upon ionization, also expressed in Rydberg units and g_i is the degeneracy of the initial state.

The MQDO method has been used to obtain the wave functions required to calculate the transition matrix elements in Eqs. (1) and (3). A full description of the model is reported in our previous papers [15,27]. We therefore only give a brief summary of the MQDO method, formulated to deal with molecular Rydberg transitions. The radial parts of the MQDO wave functions are the analytical solutions of a one-electron Schrödinger equation that contains a model potential of the form

$$V(r)_a=\frac{(c-\delta_a)(2l+c-\delta_a+1))}{2r^2}-\frac{1}{r} \tag{4}$$

where a represents the set of quantum numbers that define a given molecular state. The parameter δ_a is the quantum defect, l is the orbital angular momentum quantum number and c is an integer chosen to ensure the normalizability of the orbitals and their correct nodal pattern. The radial parts of bound-state wave functions are expressed as second Whittaker functions,

$$R(r)=W_{n-\delta,l-\delta+c+1/2}[2r/(n-\delta)] \tag{5}$$

The continuum radial orbitals are also eigenfunctions of the approximate central field potential (4), and may be described by the first Whittaker functions.

$$R(r)=M_{1/ik,l-\delta+c+1/2}(2ikr) \tag{6}$$

The angular part of the MQDO functions is expressed as a symmetry-adapted linear combination of spherical harmonics such that the molecular orbitals form bases for the irreducible representations of the specific symmetry of the molecule under study. This allows us to formulate separately the radial and angular contributions to the transition matrix element given by Eq. (2), so that the oscillator strength and photoionization cross-section adopt, respectively, the following expressions:

$$f_{ij}=\frac{2}{3}\Delta E Q_{ij}|R_{ij}|^2 \tag{7}$$

and

$$\sigma=2.6891\frac{1}{g_i}\left(\frac{1}{(n-\delta)^2}+k^2\right)\frac{1}{2k}Q_{ij}|R_{ij}|^2 \tag{8}$$

Q_{ij} are the angular factors resulting from the angular integration and R_{ij} are the radial transition integrals. Eqs. (7) and (8) should be multiplied by the number of equivalent electrons in the molecular orbital from which