Study of higher excited states of some polyatomic molecules relevant for plasma physics and environment

B P Marinković
The Institute of Physics, Belgrade 11080, Pregrevica 118, Serbia, and College for Electrical Engineering and Computing, Belgrade11010, Vojvode Stepe 283, Serbia
bratislav.marinkovic@phy.bg.ac.yu

Abstract. Studies of higher excited states of some polyatomic molecules relevant for plasma physics and environment have been presented. Spectra of chlorofluorocarbons are discussed together with their influence on ozone layer depletion and global warming. Tetrahydrofuran molecule was studied by photoabsorption and electron energy loss spectroscopy while the states are assigned following extensive ab initio calculations. Nitrous oxide and hydrogen sulphide spectra are discussed in terms of identifying valence and Rydberg character of excited states.

1. Introduction
Since the extensive studies of polyatomic molecular spectra by Herzberg [1] and Robin [2] there have not been attempts for systematic research of higher excited states and elucidation of electronic structure that would lead to comprehensive understanding of the behaviour of bound electrons in molecules. However, a tremendous advancement in both experimental methods and theoretical analysis of particular cases became evident through a number of published papers covering all aspects of complex molecular spectra and their manifolds. On the other hand, the role of electronically excited states of polyatomic molecules had been profoundly investigated when the specific questions had been raised, like the influence of chlorofluorocarbons (CFC) on ozone layer depletion and global warming [3-6], the replacement for plasma etching molecules [5,7] or radiation damage of DNA deoxyribose analogue molecules [8,9].

Certain difficulty in studying the higher excited states of polyatomic molecules represents the need for identification of the nature of the state; is it of valence type or Rydberg type. Very often the character of the state is mixed and it is hard to characterize it even by looking the spatial distribution of electron density function. The common knowledge that governs the experimentalist to assign the corresponding state as a Rydberg one is that a state frequency ν fits equation $hν=E_i-R/(n-\delta)^2$ where $E_i$ is the ionization potential toward which the series converges with higher n’s, R is the Rydberg constant, and δ is quantum defect of the series. It is a general rule that the oscillator strengths fall off as $n^{-3}$. Since Rydberg orbitals are largely nonbonding, the transition from bonding molecular orbital to Rydberg orbital will in general be narrower than that from the same bonding molecular orbital to an antibonding valence shell molecular orbital. For the interpretation of spectra, the determination of the Rydberg or valence shell character of the upper electronic state is of primary importance.
In this paper the studies of higher excited states for chlorofluorocarbon (CFC) molecules, tetrahydrofuran (THF) molecule and small, triatomic molecules hydrogen sulphide (H₂S) and nitrous oxide (N₂O) are highlighted.

2. Higher excited states of chlorofluorocarbon molecules

Chlorofluorocarbon molecules under photolysis are a source of atmospheric radicals and therefore are widely recognized to contribute significantly to stratospheric ozone depletion. CFC molecules are also strong greenhouse gases and they usually have a residence time in the atmosphere of about 100 years and an estimated global warming potential of 10⁴. Two main mechanisms of destruction in terrestrial atmosphere have been identified, that are: UV photo-dissociation in the stratosphere and mesosphere, and electron attachment and ion-molecule reactions in mesosphere. Comprehensive studies of these molecules and their influence on global warming have been performed by N. J. Mason and coworkers. Dichlorodifluoromethane (CCl₂F₂) molecule has been investigated by Limão Vieira et al [3] who determined the photo-absorption cross sections using synchrotron radiation in the range 5.5 – 11 eV. The electronic state assignment had been proposed for several observed bands incorporating both valence and Rydberg transitions. The strongest peak was found at the energy of 9.801 eV and was assigned as 4p Rydberg transition from 4b₂ molecular orbital and quantum defect of 1.65. The measured cross-sections were used to derive the photolysis rate and lifetime of this molecule as a function of altitude in the terrestrial atmosphere.

Eden et al [4] studied photoabsorption in CF₃Cl and other fluro-alkanes at high-resolution in the energy range 3.9 – 11.8 eV. The source of this molecule is purely anthropogenic and it is banned under terms of Montreal Protocol. The authors identified a valence state with the maximum cross section of 0.019 Mb at energy of 7.90 eV and two Rydberg type states assigned to the nₛ and nₚ series with the peaks at 9.679 eV and 10.63 eV with cross sections of 34.06 Mb and 13.07 Mb, respectively. Kitajima et al [5] studied electron energy spectra of several halogen-containing molecules, the CF₃Cl being among them. They identified the low-lying transition as ¹A₁ → ¹E transition governed by quadruple allowed interactions. They also observed higher members of two Rydberg series converging to ionization limits 6e⁻¹ and 7a¹⁻¹.

3. Higher excited states of tetrahydrofuran molecule

The excited states of tetrahydrofuran (THF), C₄H₈O, molecule have been extensively studied by Giuliani et al [9] very recently. The THF is a five membered heterocyclic ring molecule. The electronic configuration of THF in its electronic ground state and in the C₂ᵥ formalism is: (1a₁)² (1b₁)² (2a₁)² (3a₁)² (2b₁)² (4a₁)² (5a₁)² (3b₁)² (6a₁)² (4b₁)² (1b₂)² (7a₁)² (1a₂)² (2b₂)² (5b₁)² (8a₁)² (6b₁)² (9a₁)² (2a₂)² (3b₂)² : X⁻¹A₁. The C₂ᵥ correlates unambiguously to the other lower geometries. In the C₂ point group, the C₂ᵥ a₁ and a₂ become a and b₁ and b₂ correlate to b. For the C₄ geometry, a₁ and b₁ become a' and a₂ and b₂ become a''. Ab initio calculations were used to determine vertical excitation energies of the electronic states. The equilibrium geometry of the C₂ and C₄ conformers were considered.

The lowest excited states of the molecule were identified as the series converging to the ionic ground electronic state. The 3s terms are spanning from 6.04 eV to 6.88 eV while the vertical energy for the 3s(C₂) transition is estimated to be at 6.353 eV. The 3p terms are spanning from 6.8 eV to 8.4 eV while the vertical energy for the 3p(C₄) transition is estimated to be at 7.154 eV. The 3d terms are predicted to contain transitions from both conformers (C₂ and C₄) while the spectral region extends from 7.40 eV to 8.15 eV. A broad feature was observed at 7.483 eV, not well resolved from the underlying background but which agrees with the theoretical value of 7.474 eV for the excitation of the 3d(C₂) state. Additionally two intense features are observed at 7.730 eV and 7.813 eV, the values match the predicted transition energies to two 3d(C₂) states at 7.715 eV and 7.754 eV.

A Rydberg series analysis by Doucet et al [10], who measured the electronic spectrum of tetrahydrofuran between 2000 and 1200 Å in the gas phase, reported a single ns series (δ = 0.94), two np series (δ = 0.64 and 0.52) and a single nd series (δ = 0.08).
The spectrum of higher excited states studied by Giuliani et al [9] is spanning from 8.2 eV to 10.6 eV. The transitions were attributed to the Rydberg series converging to three ionization limits, $E_i$, of both conformers; the first ionic limit being 9.433 eV, the second ionic limit at 11.512 eV and the third at 11.964 eV. There were identified 13 transitions coming from C$_2$ conformer and 17 from C$_s$ conformer that converge to the first ionization limit. Four transitions were observed only in C$_2$ conformer that converge to the second ionization limit, while one transition for both conformers was identified to belong to the third limit.

4. Higher states of some triatomic molecules

Herzberg [1] had divided the consideration of triatomic molecules into three groups: di-hydrides, mono-hydrides and non-hydrides. The mostly studied di-hydride molecule is water molecule due its importance. A comprehensive review of electron cross sections for water molecule has been given recently by Itikawa and Mason [11] while the threshold electron impact spectroscopy has been presented by Jureta [12].

If the molecule has a closed-shell ground state, then the upper Rydberg states will in general appear as singlet-triplet splitting pairs. At the Hartree Fock level, the singlet-triplet splitting is $2K$, where $K$ is the exchange integral between valence shell and Rydberg orbitals. Because of the compact nature of core wavefunction, $\psi_c$, and the extended nature of Rydberg wavefunction, $\psi_R$, $K$ will be small.

4.1.1. Higher states of nitrous oxide molecule. The electron spectroscopy of nitrous oxide molecule has been extensively performed in Laboratory for Atomic Collision Processes at The Institute of Physics (LACPIP), Belgrade [13]. Both electron energy loss and electron threshold spectra were recorded and many valence and Rydberg states as well as higher excited states were identified. Rydberg states arise not only from the excitation of electron from the most loosely bound orbital in the ground state but also exciting it from any other orbital occupied in the ground state. The stability of these Rydberg states depends on the (non-, anti-) bonding character of the orbital from which electron was excited from.

Photoabsorption spectra of N$_2$O have been extensively studied by UV sources and electron dipole spectroscopy [14]. Also, preliminary high resolution data has been recently reported between 4.13 eV (300 nm) and 11.3 eV (110 nm) [15]. Nitrous oxide does absorb in the near ultraviolet. Absorption spectrum shows two broad features followed by the series of higher excited states.

4.1.2. Higher states of hydrogen sulphide molecule. Sulphur gases are known to be precursors of sulphate aerosol particles and cloud condensation nuclei over remote parts of the oceans and could also act as a feedback mechanism in climate regulation which affects the Earth’s radiative balance by direct scattering of solar radiation. The ground state electronic configuration of H$_2$S is (1a$_1$)$^2$(2a$_1$)$^2$(1b$_2$)$^2$(3a$_1$)$^2$(1b$_1$)$^2$(4a$_1$)$^2$(2b$_2$)$^2$(5a$_1$)$^2$(2b$_1$)$^2$ X$^1A_1$. Most of the excited states are formed from the excitation of an electron from 2b$_1$ orbital. The 2b$_1$ and 5a$_1$ orbitals are nonbonding, while the 6a$_1$ orbital is anti-bonding. Since the 2b$_1$ orbital is nonbonding, the ground state of H$_2$S$^+$ with one electron removed from this orbital is expected to have nearly the same stability as neutral molecule and the same applies for Rydberg states which converge to the ground state of ion. The vibrational frequencies of neutral and ion molecule differ only slightly. That is why 0-0 bands are the strongest bands in each series corresponding to transitions from the ground stat to Rydberg states. The first excited states $^3A_1$ and $^3B_1$ are repulsive states and responsible for the broad maximum in the spectra.

The electron spectroscopy studies of H$_2$S have been performed in LACPIP Belgrade, both electron energy loss and electron threshold spectra were recorded. Energy loss spectra were recorded at higher impact energies and smaller scattering angles that favour the optically allowed transitions and at smaller impact energies and higher scattering angles where the optically forbidden states show up.
Figure 1. Electron energy loss spectrum of higher excited sates of H$_2$S recorded at 15 eV impact energy and 40° scattering angle

5. Conclusions
The higher excited states of some chlorofluorocarbon molecules, tetrahydrofuran molecule and triatomic nitrous oxide and hydrogen sulphate molecules have been presented and discussed. The electron energy loss spectrum of H$_2$S has been recorded at low impact energy of 15eV and relatively large scattering angle of 40°.

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