

ROTATIONALLY RESOLVED PULSED-FIELD-IONIZATION ZERO-KINETIC-ENERGY PHOTOELECTRON SPECTRUM OF CYCLOPROPENE

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The high-resolution photoionization and pulsed-field ionization zero-kinetic energy (PFI-ZEKE) photoelectron spectra of cyclopropene have been recorded in the vicinity of the first adiabatic ionization energy following single-photon excitation from the neutral ground state using a narrowband vacuum ultraviolet laser system. The spectral resolution of better than 0.2 cm^{-1} achieved in these spectra is sufficiently high to resolve the rotational structure. Our study includes the measurement of partially deuterated cyclopropene species to aid in the rotational analysis of the spectra as well as better understand the geometry of the cyclopropene cation. The molecular constants derived in the analysis of the spectrum provide insight in the structure and dynamics of C_3H_4^+ in its electronic ground state.

Presentation mode: lecture

Time required: 15 MINUTES min

Comment: *Please schedule on Friday or before to accommodate travel plans. Thank you.*

WATER VAPOR LINE SELF-BROADENING CALCULATIONS WITH USE OF ACCURATE VIBRATION-ROTATION WAVE FUNCTIONS

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Calculations of H_2^{16}O rotation-vibration selfbroadening and selfshifting were performed using a semi-empirical approach. The calculations were based on impact theory modified by introducing additional parameters to extend the use of empirical data.

It should be noted that previous works used wave functions, determined by the method of effective rotational Hamiltonians. This method disregarded the strong intramolecular perturbations caused by high vibration excitation and don't describe accurately spectra in high frequency region. Earlier we have shown the necessity to use more accurate wave functions than those arising from simple effective Hamiltonians. It was proposed approach where the accurate wave functions, calculated using DVR3D nuclear method were used. Wave functions were obtained with a high accuracy potential energy surface based on high quality *ab initio* calculations augmented by relativistic and diagonal non-Born-Oppenheimer corrections. These wave functions have been used to calculate dipole transition probabilities with the *ab initio* dipole moment surface of Schwenke and Partridge. In principle, the use of the accurate wave functions, obtained from global variational calculations, extends the applicability of the method up to dissociation energy of molecule.

The main feature of the present calculation is the use of a complete set of high accuracy vibration-rotation dipole transition moments calculated for all possible transitions using wavefunctions determined from variational nuclear motion calculations and an *ab initio* dipole moment surface. The calculation results well agree with experimental data.

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SOME CONSEQUENCES OF SUPERCRITICAL WATER SPECTROSCOPY: WATER DIMER AT EQUILIBRIUM

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In spite of long lasting discussion the water dimer role in atmospheric absorption and as a consequence in radiation balance of Earth remains uncertain. The main reason of the uncertainty is a very limited number of confirmed experimental spectral observations in equilibrium conditions where the dimer manifests itself. Spectroscopy of supercritical water is one kind of such observations. Experimental conditions ensure considerable fraction of the dimer in the studied sample. Such studies in IR range were undertaken by several groups. Their results are reproducible and confirm each other. However, interpretation of these spectra is embarrassed, on one hand, because of close coincidence of vibrational frequencies of the monomer and the dimer (as well as higher other water associates) and as a consequence by strong overlapping of ro-vibrational bands of these molecules and, on another hand, because of difficulties of accounting of collisional broadening and coupling of lines at that extreme conditions.

In the report we present an attempt of reanalysis of supercritical water spectra in the range of 2500-5000 cm^{-1} recorded by Jin and Ikawa¹⁻² at 650 K and pressures up to 130 atm. The goal of the analysis was spectroscopic interpretation of the spectra on the base of known to date information on the subject. Shape of water monomer spectrum was calculated by use of Adjustable Branch Coupling model and HITRAN database. Evolution of the spectrum after the monomer contribution subtraction can be qualitatively good interpreted on the base of experimental data on water dimer obtained from cold molecular beams and in He droplets. Obtained from the analysis value of the dimer equilibrium constant is in a very good agreement with known value of the second virial coefficient of water determined on the base of experiment including data at high temperatures. Possible contribution of water trimer is estimated.

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1. A. A. Vigasin, Y. Jin, S. Ikawa. *Mol. Phys.*, 106, 1155-1159 (2008).
2. A. A. Vigasin. *Mol. Phys.*, accepted (2010).

Presentation mode: lecture

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MILLIMETERWAVE CONTINUUM ABSORPTION

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Investigation of spectral properties of atmospheric gases is demanded for developing of absorption models. Such models are very important for global monitoring of the Earth's atmosphere. The majority of spectral parameters of atmospheric lines and continuum can be obtained only in laboratory experiments. Accuracy of the recovered atmospheric parameters depends directly on the accuracy of laboratory measurements. Parameterization of the continuum absorption, in particular, the water vapor continuum is one of the most difficult problems. The problem is related to yet unknown physical origin of the continuum, its weakness in comparison with absorption in regular discrete lines of water molecule, and general difficulties of the water-related measurements.

Broadband measurement of the water-related continuum by the resonator spectrometer [1] revealed strong influence of water adsorbing on resonator elements on results of the continuum parameters measurements. Analysis of the millimeter/submillimeter wave range continuum measurement methods used in the earlier studies leads to the conclusion that water adsorbing onto mirrors and related to that additional absorption could be a common factor influencing the water-related continuum parameters obtained in all well-known laboratory experiments. To overcome the problem it was proposed to use the cavity length variation method [1], which permits separation of these two types of absorptions. The method was realized using new modification of the resonator spectrometer [2]. The use of a module of two rigidly bounded maximum identical resonators, differing in length by exactly a factor of two allows accurate separation of the studied gas absorption and absorption by water adsorbed on the resonator elements. The module is placed in a chamber with temperature controlled between -30 and +60 °C which permits investigation of temperature dependence of absorption.

This report presents first results of water-related continuum absorption measurements at MM waves in the wide temperature and humidity ranges. Comparison with earlier results is presented.

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1. M.Yu. Tretyakov, M.A. Koshelev, I.A. Koval, V.V. Parshin, Yu.A. Dryagin, L.M. Kukin, and L.I. Fedoseev, *Atmos. Oceanic Opt.*, 20(2) (2007) 89-93.
2. M.Yu. Tretyakov, A.F. Krupnov, M.A. Koshelev, D.S. Makarov, E.A. Serov, and V.V. Parshin, *Rev. of Scientific Instrum.*, 80(9) (2009) 093106-1-10.

Presentation mode: lecture

Time required: 15 min

Comment: *Please schedule this talk after our first talk 'RESONATOR SPECTROMETER FOR PRECISE STUDY OF ATMOSPHERIC LINES AND CONTINUUM'*