

# High resolution Rydberg spectroscopy of 3d metal sandwich compounds: ultrasensitive probing the electron density changes in organometallic molecules

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This year chemists celebrate a centenary of transition-metal sandwich compounds representing one of the most intriguing classes of organometallics. A unique spectroscopic property of these systems consists in a presence of clearly-defined Rydberg transitions in their gas-phase absorption and ionization spectra. No other organometallic molecules reveal such features. The lower-lying Rydberg excitations in sandwiches originate at a non-bonding metal  $d_{z^2}$  orbital and their structures provide invaluable information on the ionization energies, molecular symmetries and configuration interactions. Reliable assignments of Rydberg transitions made on the basis of the corresponding term values play key roles in verification of time-dependent DFT calculations of sandwich electronic excited states [1]. The low-lying Rydberg states of sandwich molecules can work as intermediate levels in multi-photon laser ionization processes.

The resonance enhanced multi-photon ionization (REMPI) spectra provide precise electronic energies and vibrational frequencies of excited sandwich systems. The high-resolution REMPI spectra of a prototypic sandwich molecule, bis(benzene)chromium, and its deuterated analogue in the  $d_{z^2} \rightarrow 4p_{x,y}$  region reveal rich vibronic structures which are indicative of Jahn-Teller (JT) instability. The TD DFT optimization of the Rydberg-state molecule demonstrates that the JT geometry distortion is closely related to the electron density changes on the excitation. In contrast to another well-known JT system, the  $C_6H_6^+$  ground-state cation, where the largest JT contributions are provided by the vibrations involving the carbocycle, the main JT active modes in the Rydberg-state  $(C_6H_6)_2Cr$  correspond to the CH bend. This difference can be easily correlated with the nature of the degenerate molecular orbitals responsible for the JT effect.

On the other hand, the sandwich carbocycle JT distortion is revealed by the mass-analyzed threshold (MATI) spectrum of cobaltocene. The MATI peaks arise from the Rydberg levels characterizing by principle quantum numbers  $n > 100$ . The high-resolution vibronic structure of this spectrum shows the components corresponding to the out-of-plane carbocycle deformation which agrees very well with the electron density change on ionization. This change involves also the metal electrons. Accordingly, the cobaltocene MATI spectrum reveals a contribution from the skeletal  $e_1$  mode active in the second-order JT effect. These examples demonstrate that high-resolution Rydberg spectroscopy provides an extremely sensitive instrument for studying electron density changes in sandwich molecules. Recent results on other sandwich systems will be given in the presentation.

## Acknowledgements

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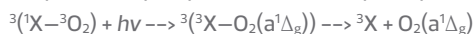
# Two-color REMPI [(1+1')+1] of the singlet oxygen $^1\text{O}_2$ arising in UV-photodissociation of van der Waals complex $\text{C}_5\text{H}_8\text{-O}_2$

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Photochemistry of the molecular oxygen is important for manifold of atmospheric and photobiological processes. Van der Waals complex of oxygen  $\text{X-O}_2$  has been shown to be a good model for the study of UV photophysics and photochemistry of the oxygen perturbed by environment [1]. The new supramolecular photoprocesses in  $\text{X-O}_2$  complexes have been revealed. One of them gives rise to the singlet oxygen  $\text{O}_2(a^1\Delta_g)$  which is interpreted to be due to supramolecular transition in complex with simultaneous change of the spin of complex partners (double spin-flip) [2]:



The singlet oxygen formation was detected with its photodissociation by the same laser pulse with formation of two atoms with specified kinetic energy measured by velocity map imaging technique (VMI). Spectral range of one-laser experiments is limited by wavelength of REMPI of oxygen atoms near 225 nm. Another way to detect the singlet oxygen is REMPI (2+1) itself in spectral range 300–340 nm [3].

In present work the one-laser approach for detection of the singlet oxygen is applied with two color REMPI [(1+1')+1] of singlet oxygen where dye laser radiation (455 – 469 nm) and its second harmonic are used simultaneously. In this approach the same excited intermediate states of  $\text{O}_2$  have been used. UV-radiation wavelength is within the spectral region of 227–235 nm where photodissociation of the Van der Waals complex of isoprene with oxygen  $\text{C}_5\text{H}_8\text{-O}_2$  is known to give rise to singlet oxygen [2]. This approach in combination with VMI has been applied to detect the singlet oxygen arising from van der Waals complex  $\text{C}_5\text{H}_8\text{-O}_2$ .

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# The vibrational structure of the $\text{NO}_3 \tilde{X}^2\text{A}_2'$ state studied by SVL DF spectrum

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We have generated  $\text{NO}_3$  in a supersonic free jet expansion, and observed laser induced fluorescence (LIF). We have measured the LIF excitation spectrum and dispersed fluorescence (DF) spectra from single vibronic levels (SVL). Vibrational structure of the DF spectrum from the vibration-less level is categorized into three parts. Region I: The  $\nu_1$  and  $\nu_3$  regions,  $\sim 1050$  and  $1500 \text{ cm}^{-1}$ , respectively, are now under active discussion, and will be discussed elsewhere. Region II: The structure in the region below  $1850 \text{ cm}^{-1}$ , excluding Region I, is relatively simple, and is the topic of the present paper. Region III: The structure above  $1850 \text{ cm}^{-1}$  is too complicated to interpret. The vibrational analysis of Region II is straightforward; the vibrational structure consists the  $\nu_4$  progression and its combination with  $\nu_1$ ,  $4^0_n$  and  $1^0_1 4^0_n$ ,  $n = 0, 1, \text{ and } 2$ , respectively, where  $\nu_1$  and  $\nu_4$  are totally symmetric stretching and asymmetric bending vibrational modes, respectively. One of the most remarkable features of the structure is the intensity pattern of the two progressions; although  $\nu_4$  is an  $e'$  mode, they display a 'regular' intensity distribution, where 'regular' means intensity gradually decreasing with increasing the  $\nu_4$  vibrational quantum number,  $n$ , above. The 'regular' structure is unusual as a progression of a degenerate mode, which usually shows an 'alternate' intensity distribution, where significant intensity is limited to even quantum numbers,  $n = 0, 2, 4 \dots$ . Some of the unusual structures of other systems have been successfully interpreted, e.g. a discussion by Herzberg, but the previous interpretations cannot be applied to the present  $\text{NO}_3$  system. To explain the unusual intensity distribution of the  $\nu_4$  progressions, we propose the following original interpretation; on the vibrationally excited  $\nu_4$  levels, the electronic and vibrational wave-functions are strongly coupled, and behave as vibronic wave-functions,  $|K; \Lambda; \nu_4, l\rangle \neq |\Lambda\rangle|v_4, l\rangle$ .

# Line shape study of oxygen B-band with CRDS in Dual-Beam configuration

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Oxygen B-band, despite its low intensity, has recently been recognized as a valuable tool in atmospheric studies. If used together with about 15 times stronger A-band, it leads to increased measurement accuracy in several applications such as determination of pressure and temperature profiles in the atmosphere, remote clouds observations and stratospheric winds detection.

The B-band is characterized by very low line intensities (below 6·10<sup>-25</sup> cm/molecule), which causes that the accurate laboratory measurements require techniques supported by an optical cavity. We present results of our recent investigations of O<sub>2</sub> B-band line shapes performed with one of the most sensitive absorption-based measurement techniques, which is cavity ring-down spectroscopy (CRDS).

We used an optical frequency comb (OFC) assisted, Pound-Drever-Hall (PDH) locked, frequency stabilized cavity ring-down spectrometer (FS-CRDS) [1]. In a present setup the probe laser beam was split into two beams of orthogonal polarizations: locking beam and actual probe beam, detuned from each other by one cavity free spectral range (FSR), similarly as in Ref. [2]. With this system we investigated the influence of the probe beam detuning from the cavity resonance, as well as its incomplete switching and phase shift of incident light during amplitude switching, on the observed pumping and decay signals. We show that this can significantly affect ring-down signals and leads to systematic errors in measured absorption coefficient. All of this can be simulated with the use of a simple analytical model [3].

The change from single to dual-beam configuration of the CRDS together with accurate switching of the probe beam enabled a significant increase of a signal-to-noise ratio (SNR) in measured spectra. The quality of spectra, measured by quality of the fit parameter (QF) can be as high as 40000 in a single scan. This sensitivity is high enough to record the quadrupole transition T5 S6 with intensity of about 1.4·10<sup>-30</sup> cm/molecule.

Transitions from the O<sub>2</sub> B-band located near 690 nm were studied. Detailed analysis of P9 P9 line shape shows that its accurate modelling even in the pressure range as low as 10 Torr (1.3 kPa) requires accounting for the effects of speed-dependence and the Dicke narrowing [4] simultaneously. For the P1 P1 line, measured in the pressure range up to 24 Torr (3.2 kPa), this is even more clear.

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# LIF Spectrum of a $^1\Sigma$ species containing Si: linear SiOSi ?

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In our past SiCN investigation [1], we found unknown bands with  $^1\Pi - ^1\Sigma$  rotational structure in the laser induced fluorescence (LIF) excitation spectrum of SiCN. Dispersed fluorescence (DF) spectra from single vibronic levels have fairly long progressions with very harmonic structure, but no hot-band structure. From the rotational constants, the spectral species may possibly be attributed to SiOSi. The most stable geometry of the ground electronic state is reported to be cyclic by CCSD(T)/cc-pVTZ level calculation [2]. Our CCSD(T) calculation with arg-cc-pCVTZ indicates a linear geometry,  $^1\Sigma_g^-$ , lying  $\sim 2,000$   $\text{cm}^{-1}$  above this lowest cyclic structure. More advanced calculations by CAS-SCF and MR-Cl indicate that the most stable cyclic geometry correlates to  $^1\Delta_g$ , which is the ground electronic state, and the  $^1\Sigma_g^-$  state is the lowest excited state, lying  $\sim 800$   $\text{cm}^{-1}$  above the  $^1\Delta_g$  state. For the ground electronic state consisting of the cyclic and  $^1\Delta_g$  linear geometries as the two minima, our calculation predicts a strange potential energy surface: the state has a  $\sim 1,000$   $\text{cm}^{-1}$  barrier from the cyclic structure to the linear geometry. In contrast, the  $^1\Sigma_g^-$  state is predicted to have a linear structure as a single minimum. At present, we postulate that our unknown spectrum may be attributed an electronic transition from the low-lying  $^1\Sigma_g^-$  state to a  $^1\Pi$  electronic state. More precise computational studies are currently underway.

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