

Infrared spectrum and intermolecular potential energy surface of the CO–O₂ dimer

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Only a few weakly-bound complexes containing the O₂ molecule have been characterized by high resolution spectroscopy, no doubt due to the complications added by the oxygen molecule's unpaired electron spin. Here we report an extensive infrared spectrum of CO–O₂, observed in the CO fundamental band region (2150 cm⁻¹) using a tunable quantum cascade laser to probe a pulsed supersonic jet expansion. The rotational energy level pattern derived from the spectrum consists of stacks of levels characterized by the total angular momentum, J , and its projection on the intermolecular axis, K . Five such stacks are observed in the ground vibrational state, and ten in the excited state ($v(\text{CO}) = 1$). There are two separate groups of stacks, with no observed transitions between them. The groups correspond to different projections of the O₂ electron spin, and correlate with the two lowest fine structure states of O₂, $(N, J) = (1, 0)$ and $(1, 2)$. The rotational constant of the lowest $K = 0$ stack implies an effective intermolecular separation of 3.82 Å, but this should be interpreted with caution since it ignores possible effects of electron spin. The experimental energy levels enable us to predict the microwave and millimeter wave spectra of CO–O₂.

A new high-level 4-dimensional potential energy surface is developed for CO–O₂, and rotational energy levels are calculated for this surface, ignoring electron spin. By comparing calculated and observed levels, it is possible to assign detailed quantum labels to the observed level stacks. The next step will be to include spin in the energy level calculation, which has not been done previously for a weakly-bound complex in which O₂ undergoes hindered rotation.

Production and study of ionic clusters by photodissociation spectroscopy

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Ionic clusters are defined as charged species A^+-L_n formed by the interaction between ions A^+ and neutral ligands L_n . These entities possess a binding energy ($10 - 10^4 \text{ cm}^{-1}$, i.e. $1.24 \times 10^{-3} - 12.5 \text{ eV}$), that lies between those of neutral clusters and those having the strongest chemical covalent bonds¹. Ionic clusters as ideal small controllable systems are important to the study of chemical reactions such as solvation processes and proton transfer². Furthermore, in the atmosphere, their condensation leads to aerosols formation that directly affect our climate³.

We will present our homemade instrument able to produce those complexes for study by high-resolution photodissociation spectroscopy. This instrument is essentially composed of (i) a pulsed supersonic expansion plasma source, to produce the desired species at low rotational temperature, (ii) a time of flight mass spectrometer which includes a single unit able to perform acceleration, bunching and gating⁴.

The first mass spectra of cationic and anionic clusters, formed from different gas mixtures, will be presented. Two different ionization methods will be compared including an electrical discharge and an electron gun. Finally, we hope to present the first photodissociation spectroscopic results.

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Unravelling non-covalent interactions in DNA-base ... Xanthine clusters

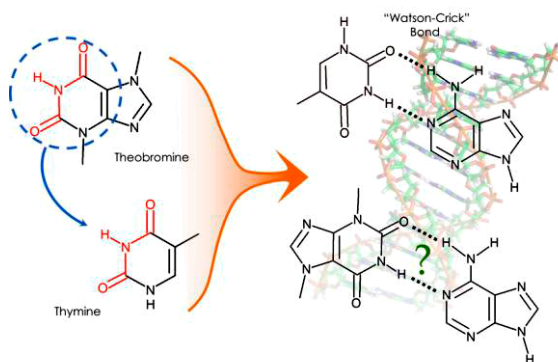
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Human metabolism commonly uses methylation processes as a tool for modulating gene expression, as changes in specific protein functions or as an epigenetic tool. In DNA, the methylation of a nucleobase immediately changes his ability for binding. Therefore, the study of the interactions between methylated bases sends light about how a structural modification changes the aggregation tendencies of DNA bases.

In the recent years, understanding the aggregation of DNA bases has been the goal of several studies, due to the relevance of such interactions for life[1,2]. However, the aggregation of DNA bases with other structurally similar compounds that are present in our metabolism, xanthine and its methylated derivatives has been rarely explored. The combination between these families is quite interesting, since some xanthines can create Watson-Crick links or analogue interactions [Fig. 1].

Here, we explore the interaction of adenine with different xanthines using a combination of mass-resolved spectroscopy and computational methods. A jet-cooled laser desorption system was used to obtain the isolated molecules and aggregates in a supersonic expansion. Next, the beam was explored using a combination of REMPI and IR/UV techniques to extract structural information. Comparison of such experimental results with the output from DFT calculations at M06-2X/6-31+G(d) and M06-2X/6-311++G(d,p) levels allowed us to assign the experimental spectra to a calculated structure. On the one hand, formation of these kind of aggregates tells us the aggregation preferences of purine bases; on the other hand, we can see the influence of the methylation in the intermolecular interactions and therefore, in the structure of the aggregates [Fig. 2].



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High-resolution spectroscopic study of the water-carbon dioxide van der Waals complex in the near-infrared range

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The jet cooled spectrum of H₂O-CO₂ and D₂O-CO₂ has been recorded in the 1.4 mm and 1.5 mm. range respectively by continuous-wave cavity ring-down spectroscopy. We observed three rotationally resolved b-type vibrational bands, two for H₂O-CO₂ and one for D₂O-CO₂. We assigned around 1000 lines in the case of H₂O-CO₂ and 120 lines for D₂O-CO₂. The vibrational assignment of those bands will be discussed but involves in terms of the (v₁,v₂,v₃) vibrational quantum numbers of the water monomer at least the (1,0,1) for H₂O-CO₂ and the (1,1,1) vibrational state for D₂O-CO₂. Even after vibrational excitation, the two vibrational bands of H₂O-CO₂ present tunneling splitting due to the internal rotation of the H₂O unit within the complex. This complex was studied before in the microwave [1] and mid-infrared [2] ranges. These studies and our work can be used to discuss the influence of vibrational excitation on internal rotation through tunneling mechanism. Finally the missing of one tunneling component for the vibrationally excited state of D₂O-CO₂ will be discussed.

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