



INFRARED SPECTROSCOPY OF GAS PHASE CLUSTER IONS

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Ai miei genitori,
con affetto e riconoscenza

Abstract

The geometric and electronic structure of mass-selected gas phase cluster ions has been studied by vibrational spectroscopy in the spectral region from 500 to 2000 cm^{-1} . Mass-selected cluster ions were stored in a helium filled radio frequency hexadecapole ion trap and excited using tunable infrared radiation from a free electron laser. The photodissociation spectrum was recorded by monitoring the parent and fragment yields as a function of the excitation wavelength.

The 500–1500 cm^{-1} spectral region is particularly revealing for metal oxides, because typical vibration frequencies for metal–oxygen single bonds lie between 500 and 1000 cm^{-1} and between 900 and 1200 cm^{-1} for metal–oxygen double bonds. Metal oxides are studied in the first part of this work. An extensive study has been carried out on *vanadium oxide clusters anions*. The infrared absorption of vanadium oxide cluster anions can be grouped in three spectral regions. The infrared transitions of (i) superoxo, (ii) vanadyl and (iii) V–O–V and V–O· single bond modes are found at $\sim 1100 \text{ cm}^{-1}$, 1020 to 990 cm^{-1} , and 900 to 580 cm^{-1} , respectively. Starting with $\text{V}_4\text{O}_{10}^-$ and for larger clusters caged structures of higher symmetry are found to be exceptionally stable. Evidence for size-dependent charge localization is found for the polyhedral cage structures of $(\text{V}_2\text{O}_5)_n^-$ clusters ($n=2, 3, 4$). Even though the largest cluster anion studied here, $\text{V}_8\text{O}_{20}^-$, is still rather small, it reveals some striking similarities with the properties of a vanadium oxide single-crystal surface, making it an interesting gas-phase model for surface adsorption and reactivity studies.

For the *aluminum oxide cluster cations*, the corundum derived structure of the $(\text{Al}_2\text{O}_3)_4^+$ gas phase cluster is demonstrated not to be the global minimum. The global minimum structure has no common features with any of the known Al_2O_3 bulk phases, contrary to previous assumptions and calculations. Also the structures of smaller alumina oxide cluster cations with the $(\text{Al}_2\text{O}_3)_{1-4}(\text{AlO})^+$ composition are found to be different from bulk-derived, or “chemical intuitive”, ones. They are rather curved two-dimensional networks, based on hexagons of alternating aluminum and oxygen atoms. The evolution of the structure with cluster size can be followed spectroscopically observing that the most intense absorption band is due to vibration modes of atoms from the perimetric ring.

Furthermore, the geometric and electronic structure of *bimetallic oxide clusters* is

studied as a function of their composition. Singly substituted $(V_2O_5)_{n-1}(VTiO_5)^-$ cluster anions with $n=1-3$ are shown to form polyhedral caged structures similar to those predicted for their isoelectronic counterparts, the neutral $(V_2O_5)_n$ clusters. Upon systematic exchange of V by Ti atoms in $V_{4-n}Ti_nO_{10}^-$ ($n=0-3$), the structure does not change. The stress induced by the isomorphous substitution results in an increased number of unpaired electrons ($n-1$) for the Ti-rich systems, leading to a triplet ground state for $VTi_3O_{10}^-$.

Experiments in the $500-2000\text{ cm}^{-1}$ spectral region access directly the strong proton transfer modes, water libration and bending modes, and the ammonia bending mode. These modes are particularly sensitive to intermolecular coordinations and their study offers a privileged view on solvation networks. Solvated ions are studied in the second part of this work. Results for the *protonated ammonia clusters* $NH_4^+(NH_3)_n$ agree satisfactorily with recent calculations. They show that the fundamental frequency of the proton transfer in the $n=1$ cluster is more than 200 cm^{-1} lower than previously predicted. Surprisingly, evidence for proton transfer is also found in the $n=4$ cluster, contrary to any expectation. The first solvation shell clearly closes at $n=4$.

The evolution of the water solvation network is studied for two systems. The spectra of $SO_4^{2-}\cdot(H_2O)_n$ dianions ($n=3-24$) represent the first infrared spectra of *multiply-charged anions* in the gas phase. They show four main bands assigned to two vibrations of the dianionic core, the water bending mode, and solvent libration. The triply degenerate SO_4^{2-} antisymmetric stretch vibration probes the local solvent symmetry, while the solvent librational band is sensitive to the hydrogen bonding network. A highly symmetric structure is found for the $n=6$ cluster and closure of the first solvation shell is found at $n=12$. The spectra of the *water cluster anions* $(H_2O)_n^-$, $n=15-50$, show signals in two frequency regions centered around 700 cm^{-1} and $1500-1650\text{ cm}^{-1}$, corresponding to water librational and bending motions, respectively. The bending feature associated with a double-acceptor water molecule binding to the excess electron is clearly seen up to $n=35$, but above $n=25$ this feature begins to blue-shift and broaden, suggesting a more delocalized electron binding motif for the larger clusters in which the excess electron interacts with multiple water molecules.

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