

# Nanostructures and impurity centers in cryogenic environments

The physics and chemistry of impurity centers and nanostructures is currently one of the most active areas of condensed matter research. Low temperatures create favorable conditions for studying quantum effects and physico-chemical processes at the atomic level. Moreover, these studies are associated with the development of various fields, ranging from the study of reactions occurring in interstellar space to the development of new materials with advanced properties, in particular, those used in organic semiconductors, optoelectronic devices, etc. This special issue presents the variety of materials being studied under the novel conditions provided by nanostructures generated in the gas phase and by the more conventional condensed phase environment of low cryogenic solids. Readers will come in touch with He nanodroplets, solid and liquid Rare Gas structures including nanoclusters. A number of species themselves and their interaction to one another and with the environment were studied, some articles cover another line of research — the influence of ionizing radiation. The majority of these contributions very effectively rely on input from quantum chemical calculations to provide powerful insight into the spectroscopic observations made under low-temperature conditions. The experimental approach comprises a variety of advanced methods — synchrotron radiation methods, laser optical methods including laser imaging techniques, supersonic jet cluster generation, formation of impurity helium clusters in superfluid helium, and numerous matrix isolation methods. Of course, it is impossible to cover the entire field in one issue, but we hope to give readers an impression of cryogenic studies of impurity centers and nanostructures, which have become one of the objects of modern physics and chemistry.

The article by V. Mykhaylovskyy and V. Sugakov considers such an interesting phenomenon as low-temperature self-oscillations of temperature and component concentration in methane ( $\text{CH}_4$ ) exposed to an electron beam. This theoretical study is related to the problem of the existence of complex organic molecules (COMs) in the gas phase of cold molecular clouds as well as to the problem of cryogenic methane moderators of neutron operation. In this paper, the authors study the effect of a reduction in the number of  $\text{CH}_4$  molecules due to their transformation into methyl and other molecules on the self-oscillations. It is shown that methane degradation leads to a decrease in the number of self-oscillation cycles, and at a high rate of degradation of methane molecules and radiolysis products, self-oscillations do not occur. Chemical reactions of silane ( $\text{SiH}_4$ ) with nitric oxide (NO) in solid Ne studied by Sheng-Lung Chou *et al.* are of fundamental interest to astrophysics especially when induced by VUV radiation. It was found that the synchrotron radiation at 130 nm produced a complex range of products, including  $\text{SiH}_2$ ,  $\text{Si}_2\text{H}_6$ , and various silicon oxides. The authors tentatively

identified a new species,  $\text{H}_2\text{SiN(H)O}$ , as an intermediate in the reaction of  $\text{SiH}_3$  with NO. These conclusions were supported by quantum-chemical calculations and D-isotope substitution experiments. The results obtained also offer valuable information for understanding silicon-based combustion chemistry. D. V. Mifsud *et al.* focused on the solid phase radiation chemistry in crystalline  $\text{N}_2\text{O}$  ices due to its potential presence on the surfaces of cold, outer Solar System bodies. In the presented study, crystalline  $\text{N}_2\text{O}$  ices were irradiated with 2 keV electrons at different temperatures in the 20–60 K range and the radiolytic dissociation of the molecular solid as well as the radiolytic formation of seven product molecules ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_2$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$ , and  $\text{O}_3$ ) were quantified. It was found that the  $\text{N}_2\text{O}$  destruction linearly depends on temperature. The corresponding characteristics of radiolysis products formation were defined. The authors estimated the survivability of crystalline  $\text{N}_2\text{O}$  on an icy Kuiper Belt Object. The interesting temperature effect was found by O. Korostyshevskiy and co-authors in  $\text{N}_2$ -Kr nanoclusters in dense cold helium gas, with a core of Kr atoms and  $\text{N}_2$  molecules on the surface. Impurity atoms of N and O formed in a gas jet previously passed through the discharge resided in the  $\text{N}_2$  surface layers. Enhanced emissions of O atoms ( $^1S \rightarrow ^1D$  transition) and  $\text{N}_2$  molecules (Vegard–Kaplan bands) were observed when the temperature in the observation zone reached the range of 20–36 K. The effect was explained by the recombination of N atoms followed by  $\text{N}_2$  molecules formation in the state ( $A^3\Sigma_u^+$ ) with the subsequent energy transfer from excited nitrogen molecules to the O atoms enhancing their luminescence.

Polycyclic aromatic hydrocarbons (PAHs), particularly acenes, are gaining attention as candidates for organic semiconductors with advanced properties — enhanced physical stability, solubility, and superior charge transport properties due to improved molecular packing. The contribution by M. Michelbach *et al.* presents a high-resolution laser-induced fluorescence spectroscopy study of triisopropylsilylpentacene (TIPS-pentacene) and pentacene in different cryogenic environments — He nanodroplets and attached to solid rare-gas clusters (Ne and Ar). The experiments revealed distinct differences in the vibronic structures of these molecules, with TIPS-pentacene displaying pronounced vibrational progressions of low-frequency vibrational modes of the molecular side groups. The results offer insights into matrix effects and advance our understanding of TIPS-pentacene's vibronic structure, recently reported to contribute via coherent vibrational wave packets to ultrafast singlet fission processes. F. Grollau *et al.* report experimental and theoretical investigations on the equilibrium between the two tautomers 4- and 5-methylimidazole in the gas phase. Experimentally, the Helium Nanodroplet Isolation (HENDI) technique was used to isolate the tautomers, and the ratio between them was

obtained via infrared spectra. This powerful and complex method leads to the observation of cooled tautomers (0.4 K) with a ratio reproducing that of the gas phase. Sophisticated calculations were performed to fully characterize the structure, energy and vibrational modes of each tautomer. Quantum chemistry calculations also addressed the isomerisation barrier. The author concluded that the predominant tautomer is 4-methylimidazole.

Another very revealing set of studies are those comparing the solvation behavior of neutral metal atoms with their singly charged cations. The time-dependent solvation of  $K^+$  ions in He nanodroplets was investigated theoretically by F. Calvo and compared with earlier similar modeling carried out by this author for Na. The location of the sites accommodating sNa and K neutral metal atoms such as on the surface of He droplets versus the migration of these cations into the cluster is enhanced by the introduction of Xe atoms whose ionization triggers Coulomb ejection of the partially solvated  $K^+$  or  $Na^+$  cation. The complete atomistic modeling of the pump-probe double ionization process, in the case of K showed that despite the similarity of the process delayed and slower solvation occurs for K. Coulomb ejection from the fully solvated  $K^+Xe$  non-covalent complex is predicted to produce the ejection of both ions, partially solvated, leaving a bare helium droplet behind. In a related study carried out by J. Soderstrom and coauthors on Ba neutral atom and cation in solid and liquid Xe, the very different site occupancies of this atom under different ionization conditions were probed at the level of single atom/ion detection. Two groups of emission peaks, each with similar excitation spectra, photobleaching behavior, and temperature dependence, are identified that may be associated with transitions from a common excited state in a particular solid Xe matrix site. Favorable conditions are found for imaging of single  $Ba^+$  ions in solid Xe. Note, that interest in the matrix isolation spectroscopy of Ba and  $Ba^+$  in solid Xe has increased in recent years accompanying work on the search for neutrinoless double beta ( $0\nu\beta\beta$ ) decay via the decay of  $^{136}Xe$  into  $^{136}Ba$ .

Infrared spectroscopy combined with matrix isolation is a very powerful tool to the characterization of molecular complexes in particular acids. J. Macyte *et al.* explored experimentally in combination with quantum chemical calculations conformers of butyric acid. Matrix isolation infrared absorption spectroscopy revealed a complex band structure of butyric acid isolated in Ar and Ne matrices suggesting the existence of multiple structural forms of butyric acid trapped in the matrices. It was found via MP2 calculations that the most stable conformer of butyric acid is the one with a nonplanar aliphatic chain, which is in contradiction with the B3LYP results, predicting the most stable conformer to have the aliphatic chain in one plane. A precise assignment of spectral bands was made due to the application of MP2 anharmonic calculations and consideration of Fermi resonance. It was concluded that three conformers with the aliphatic chain in one plane TTT, along with the nonplanar ones namely  $G^+TT$ , coexist in similar amounts isolated in noble gas matrices. I. Doroshenko *et al.* examined the influence of an Ar matrix on trapped ethanol ( $CH_3CH_2OH$ ) clusters using

FTIR spectroscopy supported by quantum-chemical calculations of optimal structure and vibrational frequencies of ethanol monomer, dimer, and trimer in vacuum, as well as in ethanol and Ar environments. It was found that the effect of the environment is manifested as a red shift of the spectral bands and a blue shift of the bands of the stretching C–H vibrations. Dimer structure was found to be the most affected by both ethanol and Ar environments. Features of explosive delayed desorption from methane-doped Ar matrices exposed to an electron beam were explored by M. A. Bludov *et al.* Radiolysis products were detected by emission spectroscopy. Based on the analysis of the concentration dependence of delayed desorption bursts and their structure, an assumption was made about the formation of  $CH_4$  clusters in Ar matrices. At a high dopant concentration of 10%, up to three consecutive bursts were recorded. A linear dependence of the total particle yield on the  $CH_4$  concentration in the range of 1–10% was found. The dynamics of intensity changes in the sequence of main flashes and their delay time were associated with thermo-concentration instability. Another effect induced by an electron beam on clusters was presented by Yu. Doronin *et al.* The authors measured the spectral distribution of the absolute differential cross-section of both ordinary and polarization ultra-soft X-ray bremsstrahlung for 0.7 keV electrons scattered on substrate-free nanoclusters of Xe. An original method based on absolute measurements of the intensity of the atom and cluster emission in the VUV and ultra-soft X-ray spectral ranges permitted to determine the cluster density in the scattering area. The study showed that the polarization component of bremsstrahlung dominates the differential cross-section for electron scattering on Xe clusters. L. A. Bulavin *et al.* presented useful information on the thermophysical properties of Ar and  $H_2O$ . They analyzed dependences of the isobaric heat capacity coefficients  $(\partial S / \partial T)_p$  versus the temperature  $T$ , pressure  $P$ , and chemical potential  $\mu$  in the liquid state along their liquid–vapor and liquid–solid coexistence curves. The last two articles of this issue demonstrate the role of ionic centers in the complex compounds  $K_2CuCl_3$  and  $LiB_3O_5:Ag$ . The absorption spectrum of a thin  $K_2CuCl_3$  film was studied by E. N. Kovalenko *et al.* in the spectral region of 2–6 eV. The analysis of the spectrum revealed the cationic nature of excitons in the  $K_2CuCl_3$  compound. The exciton spectrum of  $K_2CuCl_3$  was interpreted based on transitions in the  $Cu^+$  ion. The authors demonstrated the one-dimensional character of excitons in  $K_2CuCl_3$ . V. T. Adamiv *et al.* explored low-temperature luminescence of  $LiB_3O_5:Ag$  glass excited by synchrotron radiation with  $\lambda_{exc} = 45$  nm. Their measurements of excitation spectra along with luminescence revealed band associated with centers based on  $Ag^+$  ions that occupy the  $Li^+$  sites, as well as bands associated with centers based on  $Ag_2^+$  and  $Ag_3^+$  conglomerates.

We cordially thank all the authors for their contributions to the issue!

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