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Book Review

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Molecular Cryospectroscopy. Advances in Spectroscopy. Volume 23
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One hundred and two years ago, Sir William Ramsey's discovery of argon marked a milestone in the exploration of the periodic system of the elements. Since this time, noble gases have surprised us with many unexpected properties, the suprafluidity of liquid helium close to 0 K and the chemical reactivity of xenon and krypton being prominent examples. Condensed noble gases have found widespread application in matrix isolation spectroscopy, which has almost become a routine analytic tool. Somewhat less well known is the fact that liquid noble gases (and also other liquefied gases such as nitrogen, oxygen, or methane) have found application as solvents for spectroscopic studies at cryogenic temperatures. While the solubility of most substrates is very low in these solvents, this is compensated for by their extreme transparency both in the UV/Vis and in the infrared regime. Monoatomic noble gases simply do not have any infrared absorptions, which makes it possible to use long optical pathlengths. Spectroscopy using liquid gases—'Cryospectroscopy'—is now used increasingly regularly as a tool to characterize highly reactive reaction intermediates and to examine weak interactions between molecules. Thus the centenary of the discovery of argon was motivation for a number of Russian researchers in the group around M. Bulanin, St. Petersburg, to make their experiences in developing cryospectroscopy available to the scientific community in a book *Molecular Cryospectroscopy*, published by Wiley in the series *Advances in Spectroscopy*. The book is divided into eight chapters, seven of which stem from the Russian group of authors. In these seven chapters, the methodology, basic concepts, experimental apparatus and physics of cryosystems, and some applications are described. In an appendix, some physical constants of liquefied gases and solubilities of a series of substrates in them are given. The eighth chapter was written by M. Poliakoff and J. J. Turner from Nottingham, UK, and focuses on the application of cryospectroscopy in the characterization of organometallic reaction intermediates.

After a brief introduction by M. Bulanin, in which the concept of cryospectroscopy is explained, the experimental technique is described in detail in the first chapter, written by V. Bertsev. This chapter should be of great use to anyone wishing to get involved in cryospectroscopy, as the design of several types of spectroscopic cell with different geometries of the optical path, useful for different applications, is depicted and described. In particular the detailed sketches of the cells should enable the newcomer to quickly set up his own equipment. The chapter ends with some notes concerning sample preparation, i.e., gas condensation and sample dissolution, and the problems associated with it.

Chapter 2, 'Phase Equilibria and Spectral Analysis of Cryosystems', deals with the problem of measuring concentrations of substances dissolved in liquid gases. One problem frequently encountered in this context is the formation of finely dispersed molecular aggregates (i.e. suspensions) upon condensation of a gas containing the sample to be investigated. This not only leads to an overestimation of sample concentration, but also to changed spectroscopic properties of the sample. The chapter also contains a review of the literature dealing with the solubility of various substances in different liquefied gases followed by a brief theoretical consideration of the subject.

'Spectra and Intermolecular Interactions in Cryosystems' is the title of chapter 3 by M. Bulanin, N. Orlova, and G. Zelikina. Its subjects comprise the measurable quantities such as integrated intensity, bandshape and transition frequency of IR or UV/Vis transitions, and the influence of the specific cryogenic environment on them (in this context, for instance, IR band shifts in different cryogenic solvents are discussed). The second section of the chapter deals with isotropic and anisotropic Raman scattering in liquid gases. Included is a discussion of the Raman spectra of various small molecules (e.g. hydrogen, oxygen, methane) in different solvents (neat or in liquid argon) and at different temperatures.

Chapter 4, 'Vibrational Spectra of Polyatomic Molecules' (T. Kolomiitsova, D. Shchepkin), focuses on somewhat larger molecules. Solvent effects on vibrational spectra are discussed in detail, and considerable attention is paid to the theoretical background. Subsequently, topics related to IR spectroscopy, such as how to assign bands in cryospectra, anharmonic splitting of bands in the infrared spectrum in a polyatomic molecule, and how to derive the dipole moment of a given molecule from its infrared spectrum are discussed. The high resolution attainable by cryospectroscopy greatly enhances the amount of information to be gained from infrared spectra, and thus the detailed treatment, including many formulae, in this chapter seems justified.

The following chapter (K. Tokhadze) bears the title 'Spectra of Molecular Complexes'. Due to the high resolution of infrared spectra recorded at cryogenic temperatures in weakly interacting solvents, very small shifts in the infrared resonances of a weak complex relative to the uncomplexed monomer can be measured. A number of publications on complexation in liquid gases have been published, mostly by Russian authors, which are reviewed in this chapter. Thus, starting with very weak van der Waals complexes such as Ar ... HCl and more specific (directional) interaction as in HCl ... CO, the chapter also includes strong, hydrogen-bridge-bound complexes like HF ... dimethylether. Some complexes with rather unusual C–H–C hydrogen bridges as in CF_3H ... toluene are also discussed.

Chapter 6, 'Induced Spectra of Cryosystems', by A. Kouzov, deals with the observation of transitions that are symmetry- or spin-forbidden in the isolated molecules, but can be nevertheless observed in cryogenic solution due to intermolecular perturbation of the local symmetry or collective spin effects. The chapter starts with a discourse into the theory of induced spectra, after which examples of induced spectra, as reported in the literature, are reviewed.

The last chapter from the Russian group, Nonlinear Spectroscopy and Photochemistry of Cryosystems, was written by M. Bulanin and A. Burtsev. Unlike the preceding chapters, which are of interest mostly to spectroscopists, this chapter should be of some relevance for photochemists working on reactive intermediates and for laser spectroscopists. The first section focuses on nonlinear effects observable upon irradiation of liquid gases with high doses of infrared laser irradiation. Related to this is the final section of the chapter, 'Cryosystems as Active Media', in which

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attempts to use liquid noble gases, particularly liquid xenon, as a lasing medium are reviewed. The middle section gives a brief review on the use of cryospectroscopy in characterizing reactive intermediates. This section slightly overlaps with the final chapter by Poliakoff and Turner.

Following this chapter an appendix gives information about 'physical constants of liquefied gases and solubility in liquefied gases'. In ten tables physical properties of cryogenic liquids, such as critical temperature, density, vapor pressure, refractive index, polarizability, and solubility of a variety of substances in a selection of liquefied gases. But why, one has to ask, was the table of solubilities in liquid zenon omitted in this otherwise very useful section? Considering the significant solubility of many compounds in this solvent, liquid xenon is a solvent that is likely to be of increasing importance, and this table will be missed. The last chapter of the book, 'Organometallic Photochemistry in Liquefied and Supercritical Noble Gas Solution', by M. Poliakoff and J. J. Turner, leaves the realm of pure spectroscopy and focuses on the application of cryospectroscopy in the characterization of organometallic reaction intermediates. The chapter starts with a history of the application of cryospectroscopy in organometallic chemistry, then points out the differences in experimental set-up when working with organometallics (high IR extinction coefficients in metal carbonyls, therefore short optical pathlengths required). The main focus of the chapter, however, is to give examples of how to utilize cryospectroscopy in organometallic chemistry, and to show the strategies that have been applied in the elucidation of reaction intermediates. Finally, the use of supercritical fluids (scXe, $scCO_2$) in organometallic chemistry is reviewed. Although this section principally goes beyond the scope of the book (scXe at 303 K is no longer a cryosolvent!), the use of supercritical fluids as solvents in mechanistic studies is of increasing importance, and thus this excursion seems justified.

On the whole, the book is well written. It covers a wide range of literature, and as an additional bonus many Russian contributions are cited, which are otherwise not easily accessible to readers in the western hemisphere. It is unexceptional in the sense that—like every book—it contains errors, but there are few of them. (For instance, Tolhadze *et al.* (1985), cited on p. 162, does not show up in the reference list.)

The book should primarily be of interest for those working with cryospectroscopy or intending to do so, but will also be of use for matrix spectroscopists and all interested in reactive intermediates. In addition, the first seven chapters will be of relevance for physical chemists and physicists working on spectroscopy in the condensed phase, or on molecular aggregates.

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