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Book reviews

Vibrational Spectra and Structure. A Series of Advances, Volume 4; edited by J.R. Durig, Elsevier Scientific Publishing Co., Amsterdam/Oxford/New York, 1975, xvi + 300 pages, Dfl.75.00.

This volume is the fourth in a series which is devoted to discussing the applications of infrared and Raman spectroscopy. It contains four articles submitted between July 1973 and April 1974. Three of these are closely related in that they discuss spectroscopy at low temperatures. (In fact two articles deal with applications of matrix isolation techniques.) The other chapter describes applications of force field calculations.

In Chapter 1 Lester Andrews presents "Infrared and Raman Spectra of Unique Matrix Isolated Molecules". This 38 page article by a leading spectroscopist in this field is devoted almost exclusively to molecules investigated by the author. One-third of the references are to the authors own work. Nonetheless, the article is well written and the reader can get a good impression of selected studies in this area. The infrared and Raman spectra of the following matrix isolated molecules are discussed: $M^+O_2^-$, $M^+O_3^-$, $M^+O_4^-$, and $M^+Cl_2^-$ where M is an alkali metal), O_3, OF, Cl_2O and ClO_2 and their photolysis products, $XeCl_2$, $PbCl_2$, PdO_2, metal-dinitrogen species, N_2H_2, and SO_2 and its discharged species (SO_3, S_2O, O_3, S_3, S_4, S_2 and SO). The spectra of a number of isotopically substituted derivatives of the above molecules are also discussed. In addition a brief experimental section is included.

Chapter 2, "Vibrational Spectra and Structure of Plastic Crystals" by Aldée Cabana is 61 pages in length. Plastic crystals, using the authors definition, are "composed generally of spherically-shaped molecules and characterized by a remarkably small entropy of fusion and by one or more order—disorder solid—solid transitions." Following an introduction which includes a summary of low-temperature solid—state phase changes for some thirteen molecules (CO, N_2, H_2S, PH_3, CH_4, SiH_4, GeH_4, CF_4, CCl_4, CBr_4, SiF_4, SF_6, and cyclopentane) and some of their deuterated derivatives, the techniques for obtaining the vibrational spectra of these plastic crystals are described. The infrared and Raman spectra of the various phases of the above molecules are then analyzed with respect to site symmetry and unit cell considerations. Unfortunately, only one set of redrawn infrared and Raman spectra (of SiD_4) are shown in the article so it is somewhat difficult to get a good impression of the data which are obtained. The article does present a fair perspective of this field in that both the advantages and difficulties of the research are evident. In many cases the spectra obtained are incomplete and not all phases have been analyzed. In other cases vibrational spectroscopy proves to be the only technique capable of determining the orientation of molecules in their various solid phases. This chapter should be of special interest to solid state scientists investigating structural changes.

Chapter 3, "Intramolecular Force Field Calculations: Methods and Applications", is an 86 page discussion by I.W. Levin and R.A.R. Pearce. Since a comprehensive review of this topic would require a book of well over a thousand pages, it would be improper to expect this article to touch on each and every relevant subject in this area. Instead, the authors present a concise mathematical background of force constant calculations (limited to the most widely accepted valence force field) and then proceed to go through illustrative examples of calculations on water as well as on several more complicated molecules. The theory presented is all in terms of matrix mechanics so that it may be difficult for some chemists to comprehend the mathematical background. The authors do a good job of presenting example calculations, however, which should clarify possible difficulties. It is rather useful to have one article, such as this, which gathers together most of the relevant equations of normal coordinate analysis. These will prove to be most useful to beginning spectroscopists. As mentioned above, it would have been impossible for the authors to do justice to this field in the small space allotted to them, but they have done a commendable job considering this limitation. It would have been nice, however, to see two aspects discussed in greater detail. First, the harmonic frequencies of water are used in the calculations; but for larger molecules these are indeterminable and observed frequencies must be utilized. The effect of using the observed (rather than harmonic) frequencies in the calculations for the molecules could have been discussed. Secondly, very little is presented to explain why certain force constants are arbitrarily neglected. For example, for N_2F_2 the interaction constant between the N=N and N—F stretching constants is set equal to zero (which it is not). For some of the larger molecules, over half of the force constants are set equal to zero. It is, therefore, misleading to state, for example, that a 23 parameter (force constant) force field was used to calculate 117 frequencies for 17 molecules when, in fact, quite a few others were used with a preset value of zero. The authors recognize this, of course, and in their concluding remarks do comment on the problem of uniqueness of force fields. To the novice, though, the selection of force constants may remain perplexing. It must be reiterated that this is a valuable article, and the discussions on force constant transferability are especially recommended. In conjunction with other references (such as the first few of this chapter) the reader can get a fairly comprehensive view of force constant calculations.

Chapter 4 at 99 pages length is the longest and has the longest title, "Characterization of the Products of Metal Atom-Molecule Cocondensation Reactions by Matrix Infrared and Raman Spectroscopy." The authors, M. Moskovits and G.A. Ozin have wisely chosen not to review the entire area of matrix isolation spectroscopy, which is done in their first ten references, but instead (like L. Andrews in Chapter 1) selected some rather specific studies on which to concentrate. The research discussed involves the formation of metal-atom vapors at high temperatures followed by cocondensation with a reacting gas onto a surface cooled to cryogenic temperatures (4-20 K). The products are generally identified by use of infrared and Raman spectra and by noting the effect of warm-up and variation in concentration. More than a dozen spectra are shown, and other figures showing structures, warming curves, etc.

make this a nicely descriptive chapter. The systems described include the reaction of transition metals (Cu, Ni, Pd, Co, Rh) and alkali metals (Li, Na, Cs) with diatomic gases (N_2, O_2, CO, Cl_2). In several cases the effects of isotopic substitution and/or the use of mixed ligands are described (to give $Ni(C^{18}O)(^{14}N_2)(^{15}N_2)_2$ for example). Matrix site effects and molecular distortions are considered in some detail and the mode of bonding between the metals and ligands are elaborated upon. Even intensity calculations, force constant calculations, and certain thermodynamic considerations are dealt with. All in all this well-written article contains just about everything you would want to know about reactions between metals and gases in inert gas matrices.

This book is printed using offset type, which makes it possible to publish the material without too much time delay. Spectroscopists as well as chemists with interests in force constant calculations or low-temperature molecular species will find this a highly useful volume.

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The Organic Chemistry of Nickel, Volume II, Organic Synthesis; by P.W. Jolly and G. Wilke, Academic Press, New York/San Francisco/London, 1975, xv + 400 pages, $ 48.00, £ 24.

This book consists of six chapters which thoroughly treat the uses of nickel complexes in organic synthesis. The coverage is truly encyclopedic, extending from the initial discoveries in the area through papers in the literature of 1974. Over 1300 papers and 800 patents are cited. This bringing together of results from both industrial and university laboratories leads to a unified treatment of the field, and makes this book an invaluable reference source. The data are presented in great detail, and collected in extensive tables, allowing rapid visual retrieval of desired information as well as reference to its appearance in the primary chemical literature. The reactions are grouped by the type of chemical conversion involved (see below). For each reaction type, mechanistic considerations are presented and discussed critically in light of current knowledge. This combination of extensive and detailed data presentation, and broad literature and patent coverage, with critical comments on published material in a remarkably readable text makes this book outstanding.

The first chapter discusses the oligomerization, cooligomerization, polymerization, isomerization, hydrogenation and hydrosilation and hydrocyanation of olefins catalyzed by nickel complexes, as well as the oligomerization of strained olefins and alkanes. Catalyst preparation, effect of added ligands on the reaction, as well as mechanistic considerations for the various transformations are discussed in some detail. The second chapter treats the nickel-catalyzed oligomerization of alkynes, cooligomerization of alkynes with alkenes and 1,2-dienes, hydrosilation of alkynes, and the telomerization of allene in a similar fashion. Chapter three deals with the cyclodimerization,