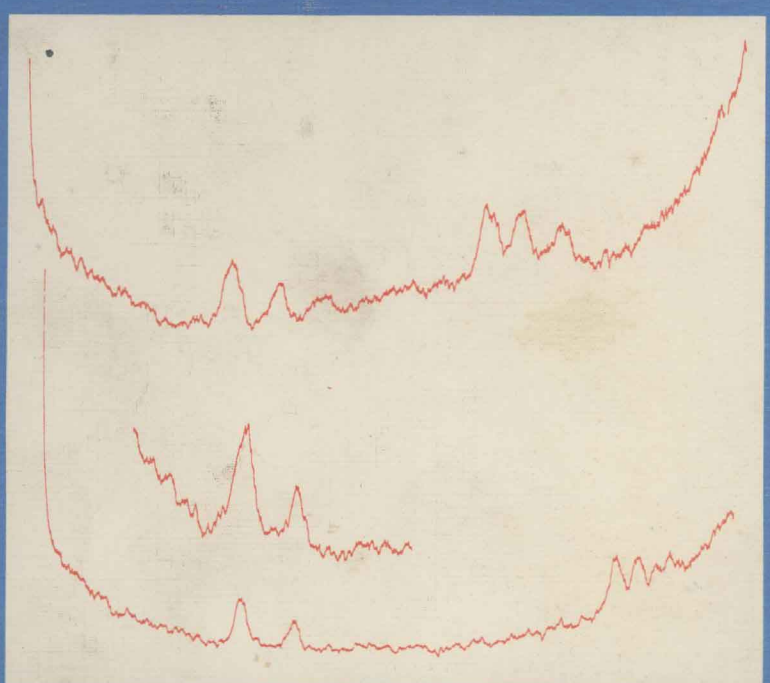
VIBRATIONAL SPECTRA AND STRUCTURE



Volume 12

edited by James R. Durig

VIBRATIONAL SPECTRA AND STRUCTURE

A SERIES OF ADVANCES

VOLUME 12

EDITED BY

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ELSEVIER – AMSTERDAM – OXFORD – NEW YORK 1983

ELSEVIER SCIENCE PUBLISHERS B.V.
Molenwerf 1
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Distributors for the United States and Canada:

ELSEVIER SCIENCE PUBLISHING COMPANY INC.
52, Vanderbilt Avenue
New York, NY 10017

ISBN 0-444-42197-1 (Vol. 12)
ISBN 0-444-41708-7 (Series)

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Printed in The Netherlands

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PREFACE TO THE SERIES

It appears that one of the greatest needs of science today is for competent people to critically review the recent literature in conveniently small areas and to evaluate the real progress that has been made, as well as to suggest fruitful avenues for future work. It is even more important that such reviewers clearly indicate the areas where little progress is being made and where the changes of a significant contribution are minuscule either because of faulty theory, inadequate experimentation, or just because the area is steeped in unprovable yet irrefutable hypotheses. Thus, it is hoped that these volumes will contain critical summaries of recent work, as well as review the fields of current interest.

Vibrational spectroscopy has been used to make significant contributions in many areas of chemistry and physics as well as in other areas of science. However, the main applications can be characterized as the study of intramolecular forces acting between the atoms of a molecule; the intermolecular forces or degree of association in condensed phases; the determination of molecular symmetries; molecular dynamics; the identification of functional groups, or compound identification; the nature of the chemical bond; and the calculation of thermodynamic properties. Current plans are for the reviews to vary, from the application of vibrational spectroscopy to a specific set of compounds, to more general topics, such as force-constant calculations. It is hoped that many of the articles will be sufficiently general to be of interest to other scientists as well as to the vibrational spectroscopist.

Most of the recent reviews in the area of vibrational spectroscopy have appeared in other progress series and it was felt that a progress series in vibrational spectroscopy was needed. A flexible attitude will be maintained and the course of the series will be dictated by the workers in the field. The editor not only welcomes suggestions from the readers but eagerly solicits your advice and contributions.

James R. Durig
Columbia, South Carolina

PREFACE TO VOLUME 12

It is the editor's belief that the current volume fulfills the goals of providing critical summaries of recent work and reviewing some fields of current interest as stated in the Preface to the Series. In Chapter 1, B. I. Swanson and L. H. Jones have provided an extensive review of high resolution infrared studies of matrix isolated species, which is a relatively new and rapidly developing area. The recent high resolution studies of matrix isolated systems indicate that matrix-molecule interactions are much more complex than originally thought, and such high resolution studies should contribute greatly to a better understanding of the matrix effects in matrix isolation spectroscopy.

H. Matsuura and M. Tasumi in Chapter 2 review force field calculations for large molecules. The recent availability of fast computers makes the calculation of force constants for large molecules relatively fast. For such molecules, the number of force constants is generally much larger than the number of experimental data available and, consequently, one has to use appropriate model force fields in which constraints are imposed upon the force constants. The internal valence force field, the Urey-Bradley-Shimanouchi force field, and the group coordinate force field are reviewed, and the authors show that the group coordinate force field constants, derived systematically from n-alkanes, n-alkyl ethers, and so forth, have excellent transferability among similar molecules, and may also be used as appropriate starting force constants for similar molecules. With the recent progress in ab initio calculations of force constants, it appears that a combination of such force constants with force constants obtained from vibrational data may prove the most useful methodology for normal coordinate calculations on large molecules.

In Chapter 3, A. Y. Hirakawa and M. Tsuboi review some of the problems on the structure of molecules in the electronic excited states as studied by the resonance Raman technique. In this chapter, they describe how one derives an excited state geometry from a set of observed resonance Raman data, and briefly survey the theoretical background of the method. Some of the prospects of the method are discussed, and the difficulties which one currently faces with the method, along with possible means to alleviate them, are enumerated. This method is applicable to a molecule in its liquid state or in aqueous solution where the ro-vibronic energy levels are not usually well defined.

In Chapter 4, Wurrey, DeWitt and Kalasinsky review the vibrational

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Chapter 1

HIGH RESOLUTION INFRARED STUDIES OF SITE STRUCTURE AND DYNAMICS FOR MATRIX ISOLATED MOLECULES

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*This work performed under the auspices of the U. S. Department of Energy.

I. INTRODUCTION

Matrix-isolation techniques were originally developed as a means of trapping molecules, particularly reactive transients, in an inert cryogenic environment in order to study their properties, using, primarily, spectroscopic methods. At temperatures well below the melting point of the host matrix material, where molecular diffusion is suppressed, the complicating effects of intermolecular interactions present in the neat condensed phase are removed. The low temperatures employed result in rigid trapping environments where rotational structure and hot bands present for gaseous systems are largely eliminated. As a result, absorption spectra of matrix-isolated molecules are generally quite sharp. Lewis [1] was the first to employ matrix-isolation techniques in studying aromatic molecules doped into a rigid glassy solid. Porter [2] and Pimentel [3] were the first to develop matrix-isolation using rare gas and N_2 solids in order to stabilize transient species. Before the development of pulsed lasers and modern time-resolved spectroscopic methods, matrix-isolation offered the best opportunity to study reactive species and, as a consequence, the area progressed rapidly.

The focus of recent research utilizing matrix-isolation techniques spans several distinct topics. New methods have been developed to expand the study of transient species to include ions [4] and metal clusters [5] as well as radicals, high temperature species, and photochemical products. Following the successful application of high power infrared lasers to effect the photo decomposition of small molecules such as BCl_3 and SF_6 in the gas phase [6], there has been considerable effort to study IR laser-induced chemistry of matrix-isolated molecules. Poliakoff and Turner [7] have recently reviewed the area of infrared laser photochemistry in matrices. One of the most exciting recent developments has been the study of vibrational energy transfer and relaxation in matrices. Vibrational energy relaxation rates have been obtained using both time-resolved absorption and emission measurements following Q-switched laser excitation of selected vibrational modes. Legay, who pioneered the area of vibrational energy relaxation studies in matrices, has provided an excellent early review [8]; Poliakoff and Turner [7] have discussed more recent energy transfer results that bear on IR laser photochemistry in matrices.

The underlying premise in many MIS studies is that guest-host interactions are minimal and, therefore, the molecular properties of the isolated species should be similar to those in the gas phase. For most systems, particularly stable molecules isolated in inert gas lattices, this approximation is reasonable. Indeed, many believe that the vibrational frequencies obtained

for neon matrix-isolated molecules, where the shift is usually negligible, are more reliable than those obtained from gas phase studies where rovibrational structure and hot bands complicate the spectra. Matrix studies of several diatomics and a few other small molecules have shown evidence for rovibrational structure indicating that the intermolecular potentials hindering molecular rotation are quite small. Until recently, molecular rotation was the only dynamic process that has been well studied for matrix isolated species. Experimental results and the theories developed to explain molecular rotation in matrices have been reviewed by Hallam [9] and Barnes [10].

Guest-host interactions, while weak, perturb the trapped species in a number of ways. First, the vibrational frequencies and energies of electronic transition are rarely the same for a matrix-isolated molecule as they are in the gas phase. The gas-to-matrix frequency shifts for molecular vibrations can be quite large even for some stable species such as the hydrogen halides [10]. Turner has also shown that direct interactions between a photo product and a host matrix often can occur giving rise to substantial perturbation of the electronic states [11].

A more subtle matrix effect is the occurrence of multiple trapping sites, each with their own discrete molecular spectra. Vibrational frequencies are relatively insensitive to the nature of the trapping site, although electronic transitions can be significantly perturbed. The number of examples where different trapping sites have been studied by vibrational spectroscopy have, until the present work, been sparse. Turner [12] has shown that $Fe(CO)_4$ occupies several discrete sites and that IR laser-induced rearrangement is site selective. Matrix-molecule interactions can also give rise to splitting of degenerate modes when the environmental symmetry of the trapping site is lower than that of the isolated molecule. Until the present high resolution studies, it has been difficult to separate the effects of multiple trapping sites from the possible occurrence of a site symmetry splitting. Hallam [9] has provided an excellent early review of matrix effects and Barnes [10] has discussed the theories which have been developed to model matrix-molecule interactions.

The early vibrational spectroscopic studies of matrix effects were limited by the spectral resolution employed (typically 1 cm^{-1}). Recent high resolution infrared studies employing diode laser and Fourier transform systems have shown that matrix-molecule interactions are much more complex than originally thought. Gunthard and Dubbs [13,14] have pioneered the use of diode laser spectrometers in studying matrix-isolated molecules. In addition to obtaining accurate line shapes [13], they were able to observe hole burning for one isomer of trans-difluoroethane isolated in argon [14]. High resolution experiments of this kind, while sparse, offer a direct means of

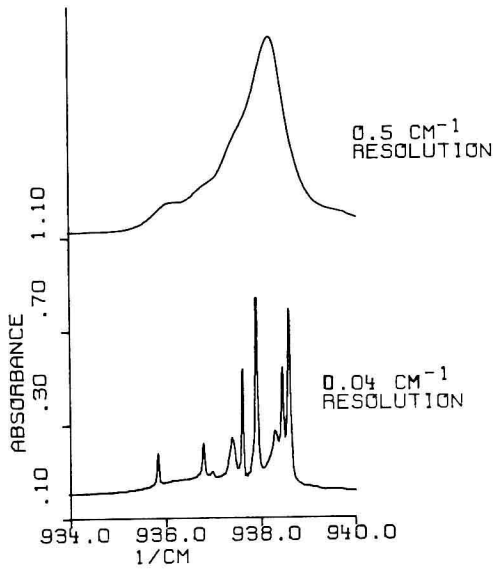

FIG. 1. ν_3 region for Ar/SF_6 = 10,000 at 9°K after 30°K anneal; 0.5 cm^{-1} vs. 0.04 cm^{-1} resolution.

obtaining the homogeneous line shapes and, by comparison with the absorption line shapes, information concerning inhomogeneous broadening. Dubost et al. [15] and Poliakoff et al. [16] have also observed high resolution absorption spectra using laser diode spectrometers as a means of unraveling matrix-molecule dynamics.

We have employed an FTIR spectrometer capable of 0.035 cm^{-1} resolution to study several high symmetry molecules in a variety of host matrices [17-22]. In Fig. 1 we present the ν_3 mode of SF_6 (asymmetric S-F stretch) isolated in an argon matrix and observed at 0.5 and 0.035 cm^{-1} resolution. At 0.5 cm^{-1} resolution a single asymmetric line is observed which splits into several discrete sharp peaks when observed at 0.035 cm^{-1} resolution. The detailed fine structure observed for SF_6/Ar matrices at high resolution demonstrated that even for nonpolar highly symmetric molecules in a high symmetry host lattice, several distinct trapping sites as well as site symmetry splittings can occur. We hope to show that complexity in the infrared absorption spectra of matrix isolated molecules is the rule rather than the exception and that such fine structure can provide a wealth of information about matrix-molecule interactions.

During the course of our studies of matrix-isolated molecules, we have relied heavily on following the temperature dependence of the absorption fine

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