COBLENTZ SOCIETY NEWSLETTER

Mailing No. 36

November 15, 1967

I. Nominations to Board of Managers

Two new members of the Board of Management are to be elected early in 1968, replacing Nelson Fuson and Forrest Mortimer whose terms expire. Board members continuing are Freeman Bentley (1969), W. G. Fateley (1969), R. E. Kagarise (1970), and Samuel Krimm (1970). Earl Plyler, chairman of the nominating committee, is anxious to have suggestions from the membership for possible nominees. Names should be sent before December 1 to:

Dr. Earl K. Plyler
Department of Physics
Florida State University
Tallahassee, Florida

Other members of the nominating committee are Henry Morgan and Bob McDonald.

II. IR Data Retrieval Project

The program of punching IBM cards for IR spectrum retrieval (Wyandotte cards) has now been moved from Wyandotte Chemicals to ASTM headquarters in Philadelphia. Taking over responsibility for the effort is Mr. Richard Sherwood, recently added to the ASTM staff for this purpose. Mr. Sherwood's responsibility will also include the visible and ultraviolet spectra punch card system and the empirical formula indices.

Dr. L. E. Kuentzel is no longer associated with these projects. During the past 20 years, Les has devoted most of his waking hours to developing and promoting these activities. The development of chemical infrared spectroscopy has received a real impetus from Les' untiring efforts, and all workers in the field owe him a real debt of gratitude. Les was also a member of the Coblentz Board of Management for the past 6 years; his advice and counsel will be sorely missed.

III. OSRD Infrared Spectral Data Project

The purpose of this project is to implement the distribution of evaluated infrared spectra from government and private files (background on the National Standard Reference Data System is given in Coblentz Society Mailing No. 24). This effort, carried out by ASTM with technical assistance from the Joint Committee on Atomic and Molecular Physical Data, was formerly located at Wyandotte Chemical Co. but has now been moved to ASTM headquarters in Philadelphia. The current status of the project is as follows: About 13,000 spectra have been contributed; 1700 have been critically evaluated, and 650 accepted for publication. It is hoped that an initial offering of 1000 spectra will be available to interested laboratories within six months. Additional progress reports will be carried in future mailings and at the general membership meeting to be held in Pittsburgh next March.
IV. Coblentz Society Symposium at Pittsburgh

Infrared Spectrometer to Chemical Structure: A Giant Step (R. E. Kagarise, Presiding)

1:30 I. Coblentz Award

2:00 II. Good Infrared Spectra: Their Preparation: (W. J. Potts)

2:30 Their Evaluation: (C. D. Smith)

3:05 III. Problems of Molecular Structure Solved by Combined Techniques (R. A. Friedel)

3:50 IV. Infrared Structure Determination as Practiced by the Spectroscopist and the Organic Chemist: Two Points of View

3:50 A. The Organic Chemist (Prof. Pierre Laszlo)

4:10 B. The Spectroscopist (N. Colthup)

4:30 C. Rebuttal and Discussion from Floor

V. Touring the Labs

Infrared Spectroscopy at Battelle Memorial Institute

by

R. J. Jakobsen

The infrared group at Battelle consists of Jim Brasch, Yukio Mikawa, and myself. Aided by a technician we divide our time between analytical spectroscopy (35%) and spectroscopic research (65%). The analytical work is a service to the rest of the Institute and consists mainly of qualitative identifications. Due to the nature of the Institute's work, our analyses cover a wide range of problems from polymer analyses to analyses of a grease spot or a pile of dirt.

The spectroscopic research is largely governed by our interest in the study of weak chemical bonds and intermolecular forces. Because of the equipment available and the nature of the problems, this research naturally divides itself by spectral region, i.e., (1) far-infrared research and (2) mid-infrared work using a diamond-window high-pressure cell.

In the past we have studied both mercuric halide vibrations and interactions of polar molecules in the far-infrared region, but now our research in this spectral region is entirely on hydrogen bonding. After completing the assignment of the hydrogen bond stretching vibration of a group of phenols, we attempted to do the same for a group of alcohols, but met with little success. We had to use the far-infrared spectra of solid alcohols in order to observe any bands and we soon found we could not make reliable assignments. We then switched to our current study of carboxylic acids. Here we have: (1) Assigned the far-infrared bands of formic and acetic acid cyclic dimers, (2) shown that all the acids but formic are dimers in the liquid state and all but formic and acetic are dimers in the solid state and, (3) proposed an assignment for both formic acid polymer and acetic acid polymer. We are currently finishing a complete assignment of propanoic acid (both mid- and far-infrared) which we
are using as our model compound because it is the first acid that we have found that is a dimer in all physical states. With the aid of these data (which enable us to distinguish hydrogen bond vibrations from CC torsions) we are finishing the assignment of the far-infrared bands of the series of acids up to C12. From a more theoretical viewpoint, our normal coordinate analysis of dimer acids have been of great aid in the assignment of acid frequencies because the formic acid force constants were successful in predicting acetic acid frequencies and the acetic acid force constants were successful for propanoic acid frequencies. From the potential energy distributions and the Cartesian displacements we feel we now have a good picture of the modes of the hydrogen bond vibrations of cyclic dimers of acids especially the influence of substitutes on the frequencies of the vibrations. In addition we have completed a normal coordinate analysis of formic acid polymer which successfully predicted the deuteration shifts. Currently we are shifting back to the study of the far-infrared spectra of alcohols where we are extending our normal coordinate analysis of formic acid polymer to alcohol polymers. We feel this will give us the needed handle to interpret the spectra.

Our mid-infrared research started as a study of the effects of high pressure on chemical bonds and on molecular spectra. It has now changed directions to: (1) a study of polarized infrared spectra of single crystals and (2) a study of the band width of the OH stretching vibration in liquids and solids. Both of these studies utilize a diamond-window high-pressure cell to grow single crystals and now we have adapted a polarizer that gives us good polarized spectra.

Because of the ease and speed of growing single crystals in the diamond cell that are of a good thickness for spectral studies, we have embarked on a program of assigning single crystal spectra and studying crystal interactions. We have just completed ttt-cyclododecatrione for which spectra along two different crystal axes showed that the interpretation of the spectra based on the oriented gas model is valid for this molecule, but only to first approximation. We are now finishing assignments of both propanoic acid and ethanol single crystals. We have polarized spectra along different crystal axes of benzene, but due to the optical behavior of solid benzene and the factor group symmetry of benzene, we cannot tell which crystal axis is which. We soon hope to obtain X-ray data to aid us with this problem.

By far our greatest current emphasis is the study of the band width of the OH stretching vibrations of alcohols. Polarized infrared spectra of single crystals of alcohols have shown us that νOH is split into two components—one broad and one narrow. From isotopic dilution studies we determined that the splitting is due to first order or nearest neighbor coupling of the vibrations of adjacent OH groups of the polymeric chain. In addition, the decoupled OH vibration was quite narrow—in the neighborhood of 30−1. This is important because we could determine that νOH for solid alcohols was not inherently broad and the breadth was due to the coupling. A tendency towards tautomerism further increased the total band width by broadening one component of the split OH vibration. In addition, we have been able to show that such coupling does not play a major part in determining the band width of νOH in liquid alcohols. At the present time, we are investigating the generality of this behavior in other hydrogen bonded systems.

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