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INFRARED PROGRAM OF THE ORNL SPECTROSCOPY RESEARCH LABORATORY
STABLE ISOTOPES DIVISION
OAK RIDGE NATIONAL LABORATORY

INTRODUCTION

This brief survey of the infrared program of the ORNL Spectroscopy Research Laboratory, Stable Isotopes Division, is made at the request of the ORNL Policy Committee, to present to them the scope and direction of the molecular spectroscopy work so that the request for a double-beam infrared spectrometer may be better evaluated.

The primary need for this instrument is to eliminate obsolescence in the instrumentation of the infrared program. This new instrument will result in no basic changes in the infrared research program; however, it will greatly facilitate the work now in progress and will allow the use of additional experimental techniques which are presently seriously hampered by instrument limitations.

PRESENT INSTRUMENTATION

The present instrumentation in infrared consists of a thirteen year old, single-beam, Perkin-Elmer Model 12B infrared spectrometer. This was modified in 1953 to permit double passing the prism with a resulting gain in resolving power of approximately two.

REQUESTED INSTRUMENTATION

The infrared spectrometer requested is a double-beam or optical null Perkin-Elmer automatic recording spectrometer complete with source, optics, KBr windows, prisms of NaCl, LiF, and CsBr, absorption cells, linear wavelength recorder, and absolute intensity integrator.

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COMPARISON OF PRESENT AND PROPOSED INSTRUMENTATION

The following table compares the present single-beam and the requested double beam instrument:

<u>Category</u>	<u>Double-Beam</u>	<u>Single-Beam Double Pass</u>
Spectrum Range	2 to 35 microns	2 to 25 microns
Recording Time	minimum 7 minutes	minimum 30 minutes
Reduction of Data Time (2 to 15 micron region)	minimum 7 minutes	minimum about 90
Recording of Wavelengths	linear recording, direct reading	non-linear recording, not direct reading
Spectral Resolution	good	better by a factor of 2
Better Instrument for:		
Qualitative Molecular Spectroscopy	X	
Quantitative Molecular Spectroscopy	X	
Tritium Compound Study		
Instrument Resolution		X
Isolation of Spectra	X	
Solids Study		
Single Crystal	X	
Matrix	X	
Isotopic Spectra	X	
Polarized Spectra	X	
Band Intensities	X	

ADVISORY COMMITTEE COMMENTS

In its report of March 5, 1956, the Stable Isotopes Division Advisory Committee made the following comments (underscoring added) regarding the spectroscopy work:

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"The committee thinks that this group is doing very good work. The research output per man is high, especially when one considers that some of the equipment has become obsolete. This is especially true in the area of nuclear magnetic resonance equipment. The direction of this group seems to be very good and the productivity, as evidenced by the number of publications completed, appears to be increasing. The capabilities of the group in optical spectroscopy and x-rays will be a source of needed strength to the whole of ORNL. The committee is especially impressed with the work on Zeeman effect and the work on molecular spectroscopy."

PRESENT INFRARED PROGRAM

Research currently active involves basic studies in the absorption spectra of molecules in the gaseous, liquid, and solid states, of solids at low temperatures, and of molecules and ions in solid solutions. Experimental work is also devoted to obtaining precise values of frequency shifts upon isotopic substitution. Computational methods are being developed both for Oracle applications and for use with desk computers in an effort to make maximum use of the data obtained.

The general approach involves the observation and assignment of infrared absorption frequencies to modes of motion within a molecule by an experimental study of band shapes, band intensities, and band displacements upon isotopic substitutions, together with a normal coordinate analysis and comparisons with related molecules. Emphasis is also given to anharmonicity effects and band intensities, with particular reference to isotopic substitutions. The molecular force constants and interaction constants are computed from the assigned frequencies and then correlated with the structure and the electron distribution within the molecule.

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Specific problems under investigation include the following:

(a) Studies of the Spectra of Simple Tritiated Molecules:

The first experimental results to be published on the absorption spectra of tritiated molecules have been reported by this laboratory¹. NT_3 is currently being prepared and will be studied in the immediate future.

(b) Studies of the Spectra of HNCO , DNCO , HNCS , and DNCS :

The changes in the normal modes of these molecules upon deuterium substitution are such that a maximum of information may be obtained² using the mathematical techniques developed for the Oracle. In particular, evaluation of the ORNL frequency measurements has revealed a lack of reliability of certain assumptions proposed in 1949 by Torkington and students in England with respect to the mathematical solution of the normal coordinate matrix problem. This work is in progress.

(c) Studies of Certain Acyl Halides and their Deuterated Species, Including CH_3COF , CD_3COF , CH_3COCl , and CD_3COCl :

Complete vibrational assignments are being worked out as outlined above and by analogy to HCOF which has been studied already at ORNL¹.

(d) Studies of Molecules in Solid Solutions:

A novel technique has been developed in this laboratory for the preparation of solid solutions, suitable for infrared study. These solutions have certain distinct advantages in regard to absorption band widths and intensities, since the perturbations from adjacent molecules or ions may be very greatly reduced. KBr and similar ionic salts have been used as solvents (at 600°C and higher) with the result that a high temperature equilibrium may be "frozen-in" at the solvent melting point. This has permitted the spectrum of monomeric SeO_2 , TeO_2 , Li_3N , and others to be observed at room temperature. The spectra of complex ions in such solid solutions are under study, particularly complex fluoride ions which are of interest to the molten fuel reactor groups. Studies of these systems are expected to provide general data on vibrational interactions in the solid lattice and information on high temperature equilibria.

¹"Infrared Spectra of T_2O , THO , and TDO ", P. A. Staats, H. W. Morgan, and J. H. Goldstein, J. Chem. Phys. 24, 916 (1956); also, Paper B9, American Physical Society Meeting, March, 1956. "The Infrared Spectrum of TCN ", P. A. Staats, H. W. Morgan, and J. H. Goldstein, J. Chem. Phys., in press. "The Infrared Spectra of T_2O and TCN ", Paper C5, Symposium on Molecular Structure and Spectroscopy, June, 1956.

²See "The Vibrational Spectra of Formyl Fluoride and Deutero Formyl Fluoride", H. W. Morgan, P. A. Staats, and J. H. Goldstein, J. Chem. Phys., in press.

(e) Computational Problems:

In conjunction with members of the Mathematics Panel (A. C. Downing and R. Bartels), new and efficient machine methods have been devised for applying normal coordinate analyses to the experimental spectral data. These methods permit either the prediction of vibrational frequencies or the calculation of force constants from the experimental data. Further work is in progress to extend and exploit the utility of these methods, in particular to provide values of interaction constants. The extended methods allow fuller use to be made of observed isotope shifts.

It should be pointed out that these Oracle computer methods can be applied advantageously to other eigenvalue problems of physical interest. In addition, new approximation methods have been devised by us for use with desk calculators as an auxiliary aid in evaluating results.

(f) Isotopic Analysis of Heavy Water:

Despite the experimental limitations imposed by the existing infrared equipment a method for high accuracy isotope analysis of D_2O for contained hydrogen was developed and proven to be competitive with mass spectrometer techniques. It is possible that this technique may be of value to HRP³ or other groups.

COOPERATIVE MOLECULAR SPECTROSCOPY WITH OTHER ORNL GROUPS

In addition to the development with the Mathematics Panel of computational techniques pertinent to molecular spectroscopy, the following cooperative studies are currently active:

(a) Study of Fine Structure in the $Ca(OH)_2$ Crystal Vibrational Spectra:

This joint project, being carried out with W. R. Busing of the Chemistry Division, involves the polarized infrared spectra of single crystals at various temperatures, and the Raman spectra of such crystals at different orientations. The data are being used, together with the neutron diffraction results obtained by Busing and H. A. Levy, in an attempt to describe the OH^- group motions and the energy levels involved.

³See, for example, memo E. L. Compere to S. E. Beall and E. G. Bohlmann, February 26, 1954. The desired limit of error of 0.1 to 1.0% of the D_2O determination quoted by Compere is readily attainable by this technique for low activity samples and should be possible at higher levels of activity.

(b) Studies of the Deuterated Ethyl Alcohols:

This is being done in cooperation with J. G. Burr of the Chemistry Division who has prepared these compounds as part of a separate study in Radiation Chemistry.

In addition to these cooperative studies, the molecular spectroscopy group consults or has collaborated on the following projects: Organic Chemistry Group, in the use of infrared for specific analytical problems; Radiation Chemistry Group, in the interpretation of organic spectra; Biology Division, in the modification and operation of infrared equipment; former Materials Chemistry Division, in the installation, adjustment, and operation of infrared equipment. Also, the techniques mastered in the synthesis of various tritium compounds were put to use in the synthesis of HT for A. H. Snell of the Physics Division. Several emergency problems involving Y-12 Plant operations have been successfully resolved. Close liaison is also maintained with the K-25 infrared group and the research groups at the University of Tennessee.

ASSOCIATIONS WITH OTHER MOLECULAR SPECTROSCOPY GROUPS

Contact (on a personal basis) is maintained between this laboratory and numerous other workers in this country and abroad. Papers are regularly presented at the annual Symposium on Molecular Structure held at Ohio State University, and presented occasionally at other meetings.

Specifically, suggestions from this laboratory have resulted in the initiation of a high resolution study of certain bands of the formyl fluoride molecule by A. H. Nielsen at the University of Tennessee.

Other suggestions by the molecular spectroscopy group have occasioned research work on the VOCl_3 molecule and its thermochromism by F. A. Miller of the Mellon Institute, and have expedited work on pressed KBr disc technique applied to

inorganic molecules, being performed under an AEC contract by Professor Underwood of Emory University.

COMPARABLE RESEARCH PROGRAMS AT OTHER INSTITUTIONS

In the basic approach of obtaining the maximum molecular spectroscopy data by and from general isotopic substitution, only S. M. Sverdlov of the U.S.S.R. appears to be carrying out comparable studies. B. L. Crawford of the University of Minnesota has made some attempts along these lines, but has been limited by the lack of computing facilities.

The full use of the normal coordinate mathematical treatment as an aid in verifying the assignment of fundamentals is an approach in use by few other laboratories, again because of the difficulties in computation. Work of this type has been reported by D. Mann at the National Bureau of Standards and by A. Meister and F. Cleveland at Illinois Institute of Technology.

L. H. Jones at the Los Alamos Scientific Laboratory has recently become involved in the study of tritium compounds. Correspondence has been exchanged in an attempt to prevent duplication of work.

PROGRAM SUMMARY

The basic research program in the Spectroscopy Research Laboratory of the Stable Isotopes Division involves (a) a strong program on the synthesis and study of tritiated compounds; (b) the exploitation of the Oracle in the evaluation of molecular structures; and (c) the investigation and exploitation of the "freezing-in" technique for studying high temperature equilibrium in molecular systems.

Improved instrumentation has become essential in carrying on this program at an ever increasing higher technical level in both research and application.