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- submillimeter waves
- electron spin resonance
- molecular beam masers
- sulfur monoxide
- cuprous halides
- methyl fluoride

**ABSTRACT**

This report contains a bibliography of nineteen published papers. These results fall into two broad classifications: A. Millimeter and Submillimeter Wave Studies and B. Solid State Studies with ESR and ENDOR.
MICROWAVE INVESTIGATION OF MATTER

Walter Gordy


U. S. Army Research Office
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Department of Physics
Duke University

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SUMMARY OF WORK UNDER ARO GRANT DAHCO4 74 G 0034
3 November 1973 through 30 October 1976

The results accomplished during the three-year grant period are mostly reported in the nineteen published papers cited in the attached bibliography. Only a brief summary of results will be given here. These results fall into two broad classifications: A. Millimeter and Submillimeter Wave Studies and B. Solid State Studies with ESR and ENDOR.

A. Millimeter and Submillimeter Wave Studies

1. Instrumentation

Low-temperature Detectors. We have obtained a silicon bolometer which operates at 1.4 K and have compared its performance with that of the low-temperature InSb photoconducting detector already operating very successfully for submillimeter wave spectroscopy in our laboratory. The two detectors proved to be comparable in sensitivity. Although the response time of the silicon bolometer is not as rapid as that of the photoconducting detector, it is adequate for video display of the spectral lines. With this silicon bolometer, rotational lines of $^{16}$O$_2$ and $^{18}$O$_2$ in the 0.7 mm region were detected, with a signal-to-noise ratio of better than 25 to 1. Because
of the encouraging performance of the silicon bolometer, we constructed a pumped liquid $^3$He cryostat for operating a silicon bolometer at 0.30 K. Theory indicates that a significant improvement in sensitivity will be gained from this further lowering of temperature. The cryostat and associated components are now being assembled; the detector should be in operation during the proposed extension of this grant.

A low-temperature cryostat and associated microwave components have been constructed for operation of a point-contact superconducting Josephson junction as detector for millimeter and submillimeter wave spectroscopy. With niobium-niobium junctions, niobium-lead junctions, and tantalum-tantalum junctions in a video-sweep spectrometer operated in the millimeter and submillimeter wave region (100 to 400 GHz), we have observed spectral absorption lines which indicate high sensitivity and broad band operation of these detectors in this region. The accompanying photograph shows a CRO display of millimeter and submillimeter wave lines detected with the Ta-Ta junction in a broadbanded sweep spectrometer. Although our preliminary experiments are promising, there are further refinements and tests to be made before we can be sure whether this detector system is as sensitive as, or more sensitive than, the other low-temperature detectors we are now using (the Si bolometer and the InSb photoconductor).

Molecular Beam Maser. A significant improvement in the sensitivity of the beam maser has been achieved through substitution of the InSb detector for the superheterodyne detector employed in the earlier design. A supersonic-nozzle, multiple-beam source has also been designed and built. This
OCS LINES DETECTED WITH Ta-Ta JUNCTION

<table>
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<tr>
<th>f (GHz)</th>
<th>146</th>
<th>182</th>
<th>219</th>
<th>255</th>
<th>292</th>
<th>328</th>
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</thead>
<tbody>
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<td>λ (mm)</td>
<td>2.05</td>
<td>1.65</td>
<td>1.33</td>
<td>1.18</td>
<td>1.03</td>
<td>0.92</td>
</tr>
</tbody>
</table>
beam source gives an up-to-ten-fold increase in beam intensity and signal strength over that of the conventional, effusive-beam source. A Fabry-Perot cavity that combines the best features of plane-parallel and semi-confocal geometries has also been designed and built for our maser. The larger mode diameter of this cavity over that of the previous design results in substantially narrower resonances. In addition, the cavity has low insertion loss, a Q approaching the theoretical limit imposed by copper losses, and a wide tunable range of frequencies. The improvements have enabled us to achieve greater sensitivity and resolution in the millimeter wave region and to extend the operation of the beam maser to significantly higher frequencies in the submillimeter region.

Submillimeter Wave Harmonic Generation with BWO's. Point-contact crystal harmonic generators, driven by millimeter wave klystrons of moderate power (\(\sim 500\) mw), have been used in this laboratory to produce tunable microwave power usable for spectroscopy to frequencies as high as 813 GHz. Preliminary tests which make use of a 5-watt, 70-GHz carcinotron (BWO) as a driving source have shown that point-contact crystal harmonic generators can be fabricated so that the full 5 watts can be used without burnout and that this order-of-magnitude increase in drive power can be translated into an order of magnitude increase of power in the submillimeter region. We are optimistic that this technique will provide coherent, tunable sources at frequencies significantly higher than 813 GHz.
2. Submillimeter Wave Spectroscopy with the Molecular Beam Maser

High-resolution, beam-maser spectroscopy has been extended into the submillimeter wave region. The submillimeter wave maser has been used to resolve and measure the deuterium and nitrogen hyperfine structure in the $J = 1 \rightarrow 0$ transition of ND$_3$ which occurs at $\lambda = 0.98$ mm. Nuclear quadrupole coupling constants obtained are $eQ(^{14}\text{N}) = 4085.5$ kHz, and $eQ(D) = -94.0$ kHz, with the nuclear magnetic couplings $C(^{14}\text{N}) = 3.52$ kHz and $C(D) = 1.42$ kHz.

Also, the beam maser was used for resolution and measurement of the deuterium hyperfine structure of the D$_2$O transition $1_{1,0} \rightarrow 1_{0,1}$ occurring at $\lambda = 0.95$ mm. A demonstration of the signal strength and resolution achieved is provided by the figure on the following page. Corrected for hyperfine splitting, the transition frequency was found to be $v_0 = 316799347 \pm 4$ kHz. Nuclear couplings and other information are given in the paper cited in the bibliography (No. 16).

3. Stark Effect of Oxygen

The first observation of the microwave Stark effect for a non-polar molecule was made on the $v_1(1)$ line of molecular oxygen at 118 GHz. Stark shifts for voltages up to 70 kV/cm were measured. From these measurements the anisotropic polarizability of the molecule was found to be $\alpha_\parallel - \alpha_\perp = 1.12 \pm 0.07 \text{ A}^3$. 
Submillimeter-wave Molecular Beam Maser Resolution

Deuterium Splitting of the $1_{1,0} - 1_{0,1}$ Transition of $\text{D}_2\text{O}$

$\nu = 316\,799.847\,\text{MHz} \quad \lambda = 0.95$
4. Rotational Transitions of Oxygen

Rotational transitions in the non-polar oxygen molecules were observed in the submillimeter wave region. Frequencies of these transitions were combined with millimeter-wave, fine-structure frequencies in a calculation of precise rotational constants, electronic coupling constants, and internuclear distances for the isotopic species $^{16}\text{O}_2$ and $^{18}\text{O}_2$.

5. High Temperature Measurements: The Cuprous Halides

Measurements of the rotational spectra of various isotopic species of cuprous chloride, bromide, and iodide were made possible by the development of a gaseous flow system for chemically producing the monomeric cuprous halides within the microwave hot cell. Observations of rotational transitions of these molecules had not been previously made. Molecular constants for the ground state and equilibrium state were obtained for the different isotopic species of each molecule. Dunham's potential constants, which give an accurate description of the potential functions, were derived from the measurements. The observed nuclear quadrupole coupling of Br and I made possible a value for the electronegativity of monovalent Cu that is more precise than previous ones. Accurate vibrational frequencies $\omega_e$ and anharmonic constants $\omega_e x_e$ were also obtained from this study.

6. Rotational Spectrum of CH$_2$DF and the Structure of Methyl Fluoride

Measurements have been made of both a-type and b-type rotational transitions in the 75 to 450 GHz region. These observations made possible
the calculation of a substitutional structure that is based entirely on accurate microwave data. The \( r_s \) structural parameters derived from a combination of these and earlier data on the symmetric species of methyl fluoride are: \( r_{CH} = 1.100 \text{ Å}, r_{CF} = 1.383 \text{ Å}, \) and \( \angle HCH = 110^{37} \).

7. **Studies of Sulfur Monoxide in the \(^1\Delta\) and \(^3\Sigma\) Electronic States**

Measurements of rotational transitions of \( \text{SO} \) in the excited \(^1\Delta\) electronic state have been made in the millimeter and submillimeter wave region. These measurements, combined with the one line observed previously by Saito, make possible the first calculation based on high precision microwave data of the rotational constants of a molecule in an excited \( \Delta \) electronic state. Measurements on transitions of the \(^3\Sigma\) ground state have been extended into the submillimeter region. These newly observed transitions make possible the direct calculation of the significant rotational constants for the \(^3\Sigma\) state of \( \text{SO} \), including the centrifugal distortion and electronic interaction constants.

8. **Measurements of Forbidden Rotational Transitions in \( \text{PH}_3 \)**

Centrifugal distortion in phosphine can disrupt the \( C_{3v} \) symmetry, to produce a slight off-axis dipole component and extremely weak \( \Delta K = \pm 3 \) transitions. The \( \Delta J = 0, K = \pm 1 \rightarrow \pm 2 \) series has been observed by Chu and Oka in the 43-47 GHz range. We have measured the \( \Delta J = 0, K = 0 \rightarrow \pm 3 \) series in the 134-144 GHz range. Through a combination of results from both series, accurate rotational constants and structural parameters were obtained for the molecule. It should be noted that the "allowed" \( \Delta K = 0 \)
transitions yield only one of the principal moments of inertia, the one corresponding to the rotation about an axis perpendicular to the symmetry axis. The "forbidden" transitions yield the moment of inertia for rotation about the symmetry axis. Both of these moments are required for a complete solution of the molecular structure. The results will be reported at the March meeting of the American Physical Society in Atlanta.

9. **Pressure Broadening of Microwave Lines of H$_2$S**

Pressure broadening parameters of four rotational transitions of H$_2$S in the 150-400 GHz region have been measured with high-resolution microwave spectroscopy. Theoretical values for the parameters were calculated with the theory of P. W. Anderson. Good agreement between theory and experiment was obtained. These results will also be reported at the March meeting of the American Physical Society in Atlanta.

**B. Solid State Studies with ESR and ENDOR**

1. **Hyperfine Structure of $^{33}$S in Irradiated Single Crystals**

We have succeeded in measuring the hyperfine structure due to $^{33}$S in the electron spin resonance (ESR) of irradiated single crystals of cystine dihydrochloride, of cysteine hydrochloride, and of N-acetyl methionine. Measurements were made with the $^{33}$S in its natural abundance of 0.76% and at temperatures of 77°K, 200°K, and 300°K. The radicals observed in each crystal at room temperature were proved by the $^{33}$S hyperfine structure to be disulfide radicals RCH$_2$SS rather than the monosulfide radicals RCH$_2$S, as had been assumed previously. Monosulfide radicals, however,
were observed and identified by the $^{33}\text{S}$ hyperfine structure in samples irradiated at 77°K and annealed at 200°K. In crystals irradiated at 77°K and observed at that temperature without warming, only charged radicals were observed.

The $^{33}\text{S}$ hyperfine structure observed for the negatively charged cystine molecule-radical $\text{RCH}_2(\text{SS})^{-}\text{CH}_2\text{R}$ revealed that the $^{33}\text{S}$ coupling is equivalent for both sulfurs and is axially symmetric about the SS bond. This observation proved that the unpaired electron is in an antibonding SS σ* orbital with the spin density shared equally between 3p(σ*) orbitals of the two sulfurs.

We believe that the results of these studies are of significance for an understanding of radiation damage in proteins and for clarification of a number of biochemical reactions in sulfur compounds. The $^{33}\text{S}$ work was done in collaboration with an alumnus of our laboratory, D. J. H. Hadley, now Chairman of the Physics Department, Georgia State University, Atlanta.

2. ENDOR of $^{14}\text{N}$ and H in Irradiated Single Crystals of Dimethylglyoxime

Electron-nuclear, double-resonance spectra (ENDOR) for the coupling nuclei in two species of radicals formed in γ-irradiated dimethylglyoxime have been measured. The more abundant of these, with the form $\text{RC(CHR)}_2\text{NO}$, had been previously detected with ESR. With the ENDOR measurements, more accurate values were obtained for the principal values of the $^{14}\text{N}$ magnetic coupling; in addition, the $^{14}\text{N}$ nuclear quadrupole couplings were
obtained. The second radical, not previously observed, is one in which the unpaired electron interacts with two hydrogen nuclei. Analysis of the data shows that the radical form is RC(NO\textsubscript{H})CH\textsubscript{2} with the -CH\textsubscript{2} group in the molecular plane. The unpaired electron is in a \pi orbital perpendicular to the molecular plane with 67\% of the spin density on the carbon of the CH\textsubscript{2} group.

3. ESR of Free Radicals Formed by Exposure of Pyrimidine Solids to Sodium Atoms

Sodium atoms were deposited on various pyrimidine powders under high vacuum at 77\(^0\) K, and the electron spin resonance spectra of the resulting free radicals were observed. Generally, the spectra show that the electron of the sodium goes into a molecular orbital of the pyrimidine ring and the Na\textsuperscript{+} ions become attached to a carbonyl oxygen of the resulting pyrimidine anion. In 5-F uracil and 5-Cl uracil, however, the halogen is evidently abstracted by the Na to form NaF or NaCl and the neutral uracil radical. Thymine shows evidence for H-addition radicals as well as the Na\textsuperscript{+}-(thymine)\textsuperscript{-} complex. The H-source for the addition radicals may be an H\textsubscript{2}O impurity in the sample, with which the sodium atoms combine to release the hydrogen atoms. In addition to a resonance with \(g = 2.00\) from the pyrimidine anion radical, broad resonances with \(g > 2\) were observed for 5-Br uracil, 5-Cl uracil, and 5-I uracil, as well as for alloxan and cytosine. These resonances, generally unstable at room temperature, are believed to arise from electrons trapped in interstitial sites or vacancies in the lattice.
4. **Conduction Electrons in Alkali Metals**

A theory of the spin-lattice relaxation time $T_1$ for conduction electrons in liquid and solid alkali metals has been developed. The $T_1$ is expressed in terms of the dynamical structure factor which includes a Debye phonon spectrum. The normal process and the umklapp process are calculated separately. The temperature dependence of $T_1$ for sodium metal has been measured in the range of $100^\circ K$ to $600^\circ K$ and found to be in satisfactory agreement with the theory.

The $g$ shifts of conduction electrons in pure and impure alkali metals have been theoretically predicted and experimentally observed. The calculated $g$ shift for Li metal is $-6.7 \times 10^{-5}$, in good agreement with the observed value ($-6.1 \pm 0.2) \times 10^{-5}$. The value for the $g$ shift in lithium is approximately $0.3\%$ in the temperature range of $4^\circ K$ to $500^\circ K$. 
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2. "Electron Spin Resonance and Bond Structure of $\text{H}_2\text{CN},"$ Donald Banks and Walter Gordy, Molecular Physics 26, 1555 (1973).


PAPERS GIVEN AT SCIENTIFIC MEETINGS
1 April 1973 - 30 Oct. 1976
(ARO Grant No. DAHCO4 74 G 0034)

Invited Papers
   Third Colloquium on High Resolution Molecular Spectroscopy.
   Tours, France, 17-21 September 1973.
   Fifith Southeastern Magnetic Resonance Conference, Tuscaloosa, Alabama.
   Southeastern Section, American Physical Society.
   IIIrd European Microwave Spectroscopy Conference.
   IIIrd International Seminar on High Resolution Infrared Spectroscopy.
   Liblice near Prague, Czechoslovakia, 2-6 September 1974.

Contributed Papers
1. "ENDOR Studies of $^{14}$N and $^{15}$N Interactions in $\gamma$-Irradiated Crystals of Dimethylglyoxime," W. H. Nelson, F. N. Atwater, and Walter Gordy,
Contributed Papers (continued)


