A BIBLIOGRAPHY
ON MICROWAVE (ROTATIONAL) SPECTROSCOPY

by

James E. Wollrab

August 1965

U S Army Missile Command
Redstone Arsenal, Alabama
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ABSTRACT

The references listed in this bibliography include a majority of the important papers and books that are related to the development of microwave spectroscopy. General references relating to the basic concepts of rotational and, in a limited way, vibrational spectroscopy are also included. Titles of dissertations, reports which have not been published in the open literature, and abstracts of papers presented at spectroscopy symposia generally are not given. Rather than a pure chronological listing, the references have been placed under specific topic headings whenever possible. A chronological order under these headings is maintained. Since a unique classification of each article is impossible, references which do not fall directly under one of the specific topics are listed in Section XII.

Several other bibliographies are available. Townes and Schawlow compiled a complete listing up through 1954. In addition, Favero has compiled a bibliography covering 1954 through 1962, and Starck has completed one for 1945 through 1962. However, the latter two are not as generally available as might be desired. (See Section I.)

This bibliography includes a majority of the references concerning microwave spectroscopy through 1964, and a number of references from early 1965. Titles are listed to enable a better preliminary assessment of the articles. The listing is a print from IBM cards and a special notation is required in some instances. Atomic weights are given in parentheses following the atomic symbol, e.g., N(14) for N. All letters are in the upper case, e.g., L-TYPE DOUBLING is written for l-type doubling. Numerical subscripts are written on the same level as the atomic symbol, e.g., H2S is written for H2S.

Preceding some of the reference lists are very brief resumes. These are not intended to serve as reviews of each area but merely to point out some of the more important or recent progress in each area.
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Section II. INSTRUMENTATION

A majority of microwave studies have been carried out using the conventional square-wave Stark-modulated microwave spectrometer\textsuperscript{5, 11, 21, 24, 112} employing phase-sensitive detection and a reflex klystron source. Measurements have been extended from X-band up into the millimeter wave region through the use of harmonic generators and the development of high frequency tubes.\textsuperscript{45, 46, 62, 63, 89, 93, 128} Sensitivity and resolution have been improved by frequency stabilization\textsuperscript{1, 6-8} and to a greater degree by phase stabilization of the source.

The demonstration of maser principles led to their use in the study of rotational spectra. Very narrow line widths have been achieved with beam-maser spectrometers\textsuperscript{100, 113} allowing the observation of hyperfine splittings which are too small to be resolved on a conventional spectrometer. Maser action has also been used to identify weak transitions when they have levels in common with stronger lines whose quantum numbers are known.\textsuperscript{94, 106}

Although Stark effect spectrometers predominate, Zeeman effect studies\textsuperscript{32, 33, 107} have been accomplished using a variety of cell designs. Other specialized microwave spectrometers include cells with "flow-through" systems for the study of short-lived free radicals, parallel plate absorption cells for precision dipole moment measurements,\textsuperscript{72} radio frequency and microwave molecular beam devices,\textsuperscript{75, 116, 119} and high-temperature cells.\textsuperscript{31, 48, 51} Relative and absolute absorption intensities, as well as line width measurements, also require specialized system design.\textsuperscript{85, 102, 111, 141} Millimeter wave transitions are being investigated as a possible source for a millimeter frequency standard.\textsuperscript{122-126, 132-135}


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SOME PHENOMENA RELATED TO THE SATURATION OF ROTATIONAL RESONANCES IN THE MICROWAVE SPECTRUM OF COS


Section IV. THE RIGID ROTOR

Calculation and characterization of the energy levels and wave functions of the rigid rotor immediately followed the introduction of the new quantum theory.\textsuperscript{1-5} Application of group theory to the problem\textsuperscript{6,9} considerably simplifies the computational difficulties presented by the asymmetric rotor whose energy levels cannot be expressed in a closed form except for low J values. Since the formulation of the reduced energy $E(\kappa)$,\textsuperscript{8,9} the original tabulations of this parameter\textsuperscript{9,17,22} have been extended to high J values for smaller intervals of $\kappa$ through the use of high-speed digital computers.\textsuperscript{19,47,49-53} Approximate methods were also developed,\textsuperscript{11,12} particularly for near symmetric top molecules.\textsuperscript{25-27,41,42} Considerable attention has also been given to the calculation of theoretical line intensities.\textsuperscript{10,18,32}


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Section VI. MOLECULAR STRUCTURE

Most microwave structure determinations have been carried out using the general isotopic substitution formulas in terms of the equilibrium moments of inertia developed by Kraitchman. The \( r_s \) and \( r_0 \) structures have been compared and discussed regarding the equilibrium structure, and a double substitution technique has been devised to treat small coordinate \(^2\). The effects of molecular vibrations on the molecular structure and, in particular, on the inertia defect determined from microwave data have received considerable attention.


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Nuclear quadrupole interactions can perturb the rotational spectrum of a molecule which contains one or more nuclei with nonspherical nuclear charge distributions. These effects have been studied in linear, symmetric, and asymmetric top molecules\textsuperscript{19, 21} to provide information concerning the electric field gradient at the quadrupole nucleus. Second-order effects can become prominent when the quadrupole interaction is sizable or when an appropriate near degeneracy is present.\textsuperscript{100, 102, 103} In the case of an asymmetric rotor, the second-order interaction may lead to an evaluation of an off-diagonal coupling constant $X_{ij}$. Intensities of the hyperfine components have been adopted directly from atomic spectra.\textsuperscript{21, 5} Bersohn\textsuperscript{37} and Misushima and Ito\textsuperscript{48} have treated the case of three quadrupole nuclei in a symmetric rotor. Work has also been done on asymmetric rotors with two quadrupole nuclei.\textsuperscript{104–106, 109, 112} As experimental sensitivity is improved, coupling in excited vibrational states may be studied.\textsuperscript{86, 88} Interactions with an external electric field are referenced in Section X.

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Section VIII. HINDERED INTERNAL ROTATION

Studies of internal rotation by microwave spectroscopy have been favored by the relative barrier heights hindering internal rotation in methyl groups and the relatively low vibrational frequencies associated with these torsional motions. Most of the barriers for CH$_3$-X type molecules, where X represents the frame of the molecule, fall in the region from 1-4 kilocalories which allows splitting of rotational transitions by rotation-internal rotation interactions to be observed either in the ground vibrational state or in excited torsional states. The latter is usually the vibrational modes of lowest frequency and is relatively well populated.

The theoretical methods to be applied to single top molecules have been reviewed by Lin and Swalen. In most cases the problem consists of a symmetric top attached to an asymmetric frame. Extensions have been made to treat two-top molecules, asymmetric top and frame, cis-gauche-trans configurations of C-C bonds, and symmetric top molecules through excited states and Coriolis effects.

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The $J$-dependence of the inversion doubling has been treated with expressions of linear$^{20},^{47},^{59}$ and exponential dependence.$^{18},^{59}$ Interactions with other molecular vibrations have been of considerable interest in ammonia$^{29},^{53}$ and methylamine.$^{24},^{34},^{35}$ The possibility of two coupled inversion-type motions was encountered in hydrazine.$^{47},^{57}$
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