A. MOLECULAR-BEAM MICROWAVE-ABSORPTION SPECTROSCOPE

A new molecular-beam microwave-absorption spectroscope was built. It contains an antenna system that allows for an interaction length of 0.7 m between molecules and microwave radiation. It also has provisions for operating the beam source at elevated temperatures. Therefore, it will be possible to observe the absorption spectra of substances like the alkali halides, whose vapor pressures are too low at room temperature.

The system is contained in an evacuated steel cylinder that carries coils capable of creating a magnetic field of a few hundred gauss. It was successfully tested, and the Zeeman effect was observed on the absorption lines of ammonia.

The spurious pressure in the steel cylinder which is caused by molecules scattered out of the beam source was studied. A device that lowers this pressure is being built; it will also improve the heat shielding of the source if the source is operated at elevated temperature.

B. A STUDY OF THE INTERACTIONS BETWEEN TORSIONAL AND OVER-ALL ROTATIONS IN SYMMETRIC TOP MOLECULES

As part of the investigation of the interaction between the hindered internal rotations and over-all rotations in symmetric top molecules, experimental work was done on methyl silane. It has been pointed out several times in the literature that the effect of torsional oscillations is to produce a series of satellite lines for each over-all rotational line. These lines have been observed for the J = 0 → 1 transition in methyl silane; for the lower torsional states, they are in good agreement with Kivelson's treatment (1) and also with Lide and Coles' measurements (2). Because of inadequate spectroscope sensitivity, conclusions could not be drawn from the data obtained on the higher torsional levels. Changes have been made to improve the sensitivity, and it is expected that data obtained in the future will make it possible to state conclusively whether or not Kivelson's theoretical treatment is adequate for the higher torsional states.

Stark-effect measurements were also made on the various satellites of the J = 0 → 1 transition. It might be expected that, because of the increased repulsion between the methyl and the silane groups in the higher torsional states, there would be a slight increase in the dipole moment of the molecule. This qualitative prediction was confirmed. An increase of a few per cent in the dipole moment was noted between that of the lowest state and that of the seventh satellite line.
(V. MICROWAVE SPECTROSCOPY)

Plans for further work include a more thorough study of the higher satellite lines of the \( J = 0 \rightarrow 1 \) transition, and an investigation of the \( J = 1 \rightarrow 2 \) lines. Calculations were also started on the various matrix elements required to predict these lines.

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References


C. VIBRATION-INTERNAL ROTATION INTERACTIONS IN ASYMMETRIC MOLECULES

Earlier work (1) indicated that the spectrum of the \( J = 0 \rightarrow 1 \) rotational transition of methyl alcohol could only be described by our considering the effects of vibrations in the molecule. In an attempt to determine which particular vibrations, if any, contribute primarily to the observed spectrum, a new approach to the interaction problem was developed.

Inspection of the vibrational spectrum of methyl alcohol as given, for example, by Herzberg (2), reveals the following. The lower energy normal vibrations, which may be expected to be the primary interactions with the internal rotational mode, are composed of motions of the methyl group and OH bar as rigid groups. This leads to the possibility of describing the interactions by means of a model consisting of two rigid groups permitted to move relative to each other in a specified manner. Coordinates were chosen to describe these motions, and it was possible to show that these coordinates correspond closely to the normal modes as listed by Herzberg.

An extension of Dennison's continued fraction solution of the internal portion of the Hamiltonian (3) has made it possible to determine the effect of adding to the usual threefold periodic cosine potential a small sixfold term. Combination of the kinetic energy of the model mentioned above with a general expansion of the potential interaction gives a Hamiltonian which, to zero order, is found to correspond exactly to the "rigid rotor" model of our earlier work (1). Higher order terms in the Hamiltonian then have matrix elements which may be written immediately in this zero-order scheme. Numerical calculations are now being carried out to evaluate these terms, and to calculate the \( J = 0 \rightarrow 1 \) transition for comparison to the observed spectrum.

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References

1. Quarterly Progress Report, Research Laboratory of Electronics, M.I.T., April 15, 1955, p. 15.
