

THE UNIVERSITY OF MICHIGAN  
COLLEGE OF LITERATURE, SCIENCE, AND THE ARTS  
Department of Physics

Final Report

INFRARED STUDIES:

Stark Effects in HCN, CH<sub>3</sub>F, CH<sub>3</sub>I, NH<sub>3</sub> and H<sub>2</sub>O  
Hindered Rotation in H<sub>2</sub>O<sub>2</sub>  
Infrared Absorption of Matrix Isolated NH<sub>3</sub>

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## I. STARK EFFECTS IN THE NEAR INFRARED SPECTRA OF SIMPLE POLYATOMIC MOLECULES

The Stark effects observed in some polyatomic molecules have been reported separately by Paul D. Maker as Technical Report No. 1 (AFCRL 681) under this contract. The abstract from that report is given here as a summary of that work.

### ABSTRACT OF TECHNICAL REPORT NO 1

A survey has been made of Stark effects in the vibration-rotation spectra of simple polyatomic molecules. Employing a light guide type Stark absorption cell 90 cm long having front surfaced mirrors as parallel plate electrodes, fields of 120 kV/cm could be obtained with sample pressures below 1/4 mm Hg. The electrode spacing of 0.2 to 0.5 mm was evaluated by examining the fringe systems produced upon passing light through the cell perpendicular to its optical axis. For this purpose, partially transparent mirror electrodes were used. The gap was held to  $\pm 1\%$  ( $\pm 2.5$  microns). An Ebert-Fastie spectrometer of three meter focal length and equipped with a 300 line/mm grating 200 mm long afforded a resolving power in excess of 75,000 when used double passed. Liquid air cooled PbS detectors and synchronous amplifiers were used.

Measurable frequency shifts were observed in the  $\nu_3$  fundamental of hydrogen cyanide. Its large dipole moment and simple spectrum made possible the resolution and identification of all the 'M' components for the lines R(2) through P(3). Careful measurement (with a relative accuracy of  $\pm .005$   $\text{cm}^{-1}$ ) of the splittings yielded a value of  $3.001 \pm .007$  debye for the dipole moment of hydrogen cyanide in its  $\nu_3$  vibrational state. The identification of Stark components in the spectra of methyl fluoride and methyl iodide was made impossible by their dense zero field spectra. The low field Stark difference spectra did, however, show line intensities differing in a predictable way from the normal spectra. This intensity variation eliminated up to 70% of the normally observed absorption lines and could be used to advantage in making assignments in the zero field spectrum. The Stark effects observed in the  $\nu_1$  fundamental of  $\text{NH}_3$  resulted from field produced mixing of the wave functions describing adjacent inversion states and consequent violation of the  $a \leftrightarrow a, s \leftrightarrow s$  selection rule. Near degeneracies which interacted in the presence of an electric field were found to account for the bulk of the Stark signals observed in the  $\nu_1$  and  $\nu_3$  fundamentals of water vapor.

Stark effect techniques, at present difficult and applicable to only a few molecules, would become valuable new infrared tools if a significant increase in resolving power (as might be obtained by using a Fabry Perot interferometer) were available.





## II. THE DETERMINATION OF THE HINDERED MOTION IN HYDROGEN PEROXIDE FROM ITS FAR INFRARED SPECTRUM

The results of the study of the far infrared spectrum of  $H_2O_2$  have been reported by R. H. Hunt as Technical Report No. 2 (AFCRL 63-890) under this contract. The abstract given here is a resumé of that work.

### ABSTRACT OF TECHNICAL REPORT NO. 2

The torsional oscillation between the two OH groups of the hydrogen peroxide molecule has been investigated by a study of the absorption spectrum of the vapor in the far infrared. A one meter focal length vacuum grating monochromator was used to scan the region from 15 to 700  $cm^{-1}$  with an average resolution of 0.3  $cm^{-1}$ . The spectrum could be analyzed into a number of perpendicular type bands of which only the Q branches ( $\Delta K = \pm 1$ ,  $\Delta J = 0$  transitions) could be identified. The centers of the seven bands that could be recognized were at 11.43, 116.51, 198.57, 242.76, 370.70, 521.68 and 557.84  $cm^{-1}$ . These bands result from transitions between different states of the internal rotation and their identification made it possible to construct the internal rotation energy level scheme complete through the first five excited states. Relative to the ground state, these levels occur at 11.43, 254.2, 370.7, 569.3 and 775.9  $cm^{-1}$ .

Leacock and Hecht have concurrently developed a treatment of the internal motion, expressing the hindering potential function as a Fourier series in  $x$  (where  $x$  is the dihedral angle between the two OH groups). The Hamiltonian for the internal motion was solved for its eigenvalues on an IBM 709 computer. The observed internal rotation levels and transitions could be fit to better than 1  $cm^{-1}$  with the hindering potential function  $V(x) = 993 \cos x + 636 \cos 2x + 44 \cos 3x$  (where the coefficients are expressed in  $cm^{-1}$ ). This hindering potential has a cis barrier of 2460  $cm^{-1}$ , a trans barrier of 386  $cm^{-1}$ , and a minimum value at  $111.5^\circ$  from the cis configuration. In addition, a number of anomalies in the spectra were quantitatively accounted for by the theory.



### III. VIBRATION—ROTATION SPECTRUM OF MATRIX ISOLATED AMMONIA

The infrared absorption of ammonia isolated in condensed inert gases has been reported separately by Robert E. Meredith as Technical Report No. 3 (AFCRL ) under this contract. The abstract from that report is given here as a summary of that work.

#### ABSTRACT OF TECHNICAL REPORT NO. 3

An investigation of  $\text{NH}_3$  and  $\text{ND}_3$  isolated in inert gas matrices at  $4.2^\circ \text{K}$  has been made in the regions of the  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  fundamentals, and in the vicinity of the overtone  $2\nu_4$ . The spectra were scanned with spectral slit widths ranging from .1 to .5  $\text{cm}^{-1}$ , and it was found that this resolution was adequate to insure that all the observed line widths and shapes were free from instrumental broadening.

The  $\nu_2$  fundamental has been interpreted in terms of a free rotation model, with the line spacings and inversion splitting having values very close to those observed for gas phase molecules. This interpretation confirms the existence of 'E' type and 'A' type (i.e., para and ortho) ammonia, although a substantial amount of nuclear spin conversion from 'E' type to 'A' type has been found.

The interpretation of the  $\nu_1$ ,  $\nu_3$ , and  $2\nu_4$  spectra was much more difficult, since these bands were too weak to permit observation of the 'E' type spectra, and since the inversion doubling of the levels involved cannot be observed due to the broadness of the lines. It was possible, however, to determine the dependence of the lines on the ratio of inert gas atoms to ammonia molecules, and to assign the transitions involved as arising from either single isolated molecules or from ammonia complexes caused by incomplete isolation. Lines were also observed which were attributed to molecules occupying different sites in the matrix.

Argon, krypton, and xenon were successively used as matrices, and spectra obtained in each case differed only in that the vibrational frequencies were shifted to longer wavelengths as the matrix was varied. A considerable amount of experimental difficulty was encountered in obtaining spectra using krypton and xenon. This was caused by an increased scattering of the infrared radiation by these matrices, and by a weakening of the lines.



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