

RESEARCH ACTIVITIES II

Department of Molecular Structure

II-A Laboratory and Astronomical Spectroscopy of Transient Molecules

Vast, cold, and low-density space environment is a unique laboratory, whose physical and chemical conditions are rarely attained in the laboratory on Earth. The unique space laboratory is favorable to the existence of transient molecules such as molecular ions, free radicals, and unstable molecules, most of which are very exotic and nonterrestrial. These exotic transient molecules are generally difficult and challenging problems for laboratory spectroscopy. Laboratory spectroscopy may be enriched by astronomical studies on non-terrestrial transient species which represent new developments in high-resolution molecular spectroscopy. On the other hand, detailed knowledge about new transient molecules obtained by laboratory spectroscopy is essential to a deeper understanding of physical and chemical processes in space. We developed a high-sensitivity submillimeter-wave and far-infrared spectrometers suitable for high-resolution spectroscopy of transient molecules of astronomical interest. We expect that our laboratory spectroscopy may accelerate the mutually beneficial aspect between laboratory spectroscopy, and astrochemistry and astrophysics.

II-A-1 The detection of the Free Radical FO ($X^2\Pi_{3/2}$) by Microwave Spectroscopy

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The FO radical is the most fundamental halogen oxide free radical and has been studied since 1979 by high-resolution infrared spectroscopy, CO₂-LMR spectroscopy,¹⁾ diode laser spectroscopy²⁾ and Fourier transform IR spectroscopy.³⁾ A full spectroscopic characterization has been recently achieved with the detection of the fine-structure transition $^2\Pi_{1/2}-^2\Pi_{3/2}$ by FIR-LMR.⁴⁾ No pure rotational spectra have been reported in literature to date. McKellar,⁵⁾ in a Stark spectroscopy experiment, demonstrated that the electric dipole moment is exceptionally small, *i.e.* 0.0043(4) D for the $\nu = 0$ level and 0.0267(9) D for $\nu = 1$.

We detected for the first time the pure rotational spectrum of the free radical FO ($X^2\Pi_{3/2}$) by microwave spectroscopy, using a reaction of ozone with atomic fluorine. Four rotational transitions $J = 7/2-5/2$ to $13/2-11/2$ have been measured in the frequency region 219–408 GHz. All the observed transitions are magnetic dipole in character. No electric dipole transitions have been observed in this experiment. Each rotational transition is split into four components by fluorine magnetic hyperfine interaction ($I_F = 1/2$) and by Λ -type doubling. The analysis of the observed data allowed a considerable improvement of some spectroscopic parameters: $B_0 = 31539.33542(32)$ MHz.

References

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II-A-2 Microwave Spectroscopic Detection of Transition Metal Hydroxide: CuOH and AgOH

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A number of microwave spectroscopic studies on metal hydroxide molecules have been reported: alkali metal hydroxides NaOH to CsOH, alkali earth metal hydroxides MgOH to BaOH, and recently, AlOH and InOH. Linearity or nonlinearity of the metal hydroxides depend on a balance between ionic and covalent structures.¹⁾ In contrast, there has been no previous microwave spectroscopy of transition metal hydroxides, where a contribution of d orbital in transition metal influences the balance between both structures. There is a need for microwave spectroscopy of such molecules, which can supply substantial information on this problem through their structural determination.

We detected rotational spectra of CuOH and AgOH for the first time by millimeter- and submillimeter-wave spectroscopy (see Figure 1). Both molecules were directly produced in the hollow cathode discharge cell by sputtering metal from the hollow cathode made of the corresponding metal, and showed asymmetric-top a-type R-branch transitions. The deuterated species CuOD and AgOD were also observed by using D₂O adsorption on the electrode in advance of measurements. From the observed molecular constants for isotopic species of both molecules their harmonic force field and zero-point averaged (r_z) structures were derived and discussed in terms of the balance between competing ionic and covalent interactions.

References

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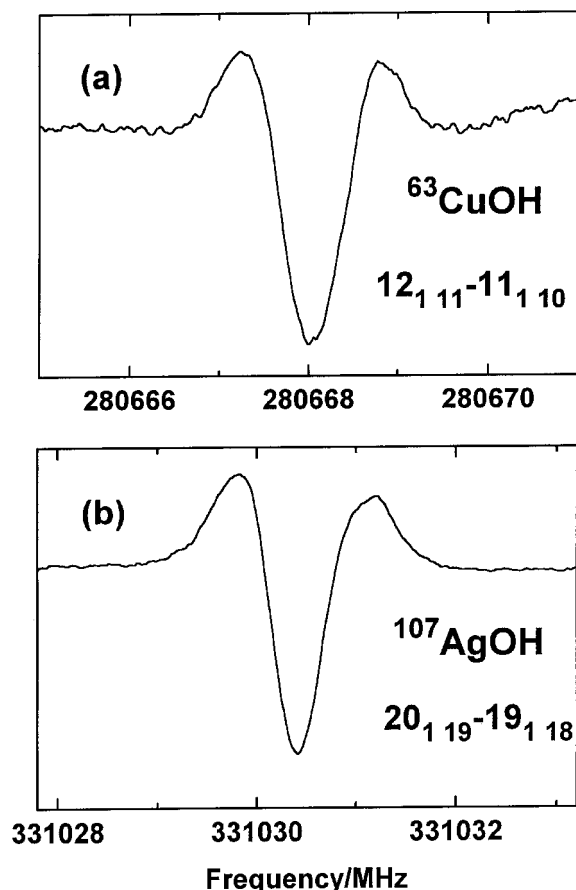


Figure 1. (a) The $12_{1,11}-11_{1,10}$ transition of $^{63}\text{CuOH}$ observed in a discharge cell, with a copper hollow cathode. (b) The $20_{1,19}-19_{1,18}$ transition of $^{107}\text{AgOH}$ observed with silver sheets inserted inside a stainless steel hollow cathode.

II-A-3 Microwave Spectrum of the Inversion-Rotation Transition of the D_3O^+ Ion: $\Delta k = \pm 3n$ Interaction and Equilibrium Structure

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In the last Annual Review we reported the experimental determination of the ground-state inversion splitting in D_3O^+ by microwave spectroscopy.¹⁾ We further measured 28 Q-branch lines including $J = K + 5$ in the 399–458 GHz region and analyzed them with previously measured R-branch and Q-branch lines, 53 lines in total. We found that inclusion of $\Delta k = \pm 3n$ interactions in the Hamiltonian was essential for a full explanation of the observed lines, with measurement uncertainty of 20 to 60 kHz. The molecular constants, including C for the 0^+ and 0^- levels, as well as the $\Delta k = \pm 3n$ interaction parameters, were derived from the fit of all data. The inversion splitting was determined to be $15.35550338(107) \text{ cm}^{-1}$, where the number in parentheses denote one standard deviation of the fit. Zero-point corrections to the rotational constants of H_3O^+ and D_3O^+ were calculated from a harmonic potential of H_3O^+ and the r_z structures were derived from the zero-

point corrected rotational constants:

$$\text{D}_3\text{O}^+(0^+): r_z = 0.9818(23) \text{ \AA}, \theta_z = 112.68(100)^\circ,$$

$$\text{D}_3\text{O}^+(0^-): r_z = 0.9830(23) \text{ \AA}, \theta_z = 112.02(100)^\circ.$$

From the shift between the r_z structures of H_3O^+ and D_3O^+ the equilibrium structural parameters of H_3O^+ was estimated to be $r_e = 0.9702(89) \text{ \AA}$, $\theta_e = 109.4(38)^\circ$.

References

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