

Friday, September 7

Morning Session

Chairman - J. DEMAISON

LF1

Theoretical Study of  $H_2O...HF$

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Two hundred and sixty points on the potential energy and electric dipole surfaces of the ground electronic state of the  $H_2O...HF$  complex have been calculated ab initio using the MBPT(4) technique. The points were chosen in order to sample a wide-range of values of the inversion and  $H_2O$  vs.  $HF$  stretching coordinates and to probe the effects of unsymmetric vibrational distortion of pyramidal and planar geometries on the electronic energies. A polynomial potential energy and electric dipole moment functions have been fitted through these points and the rotation-vibration energy levels and transition moments have been calculated using a simple nonrigid inverter Hamiltonian.

With exception for the spectral features assigned previously as the "in-plane" bending fundamentals, the agreement with experiment is fully satisfactory. We feel that this casts doubt on the assignment of these absorptions which, as a matter of fact, fit closely our theory if assigned as combination bands.

F2

# The Infrared Spectrum of MgO: A Diode Laser Study Using the Discharge-Enhanced Reaction Between Magnesium Vapour and N<sub>2</sub>O.

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We recently reported the high-resolution infrared spectra of CaO<sup>1)</sup>, SrO<sup>2)</sup>, and BaO<sup>3)</sup>. Adequate quantities of their monomers were obtained by reacting hot metal vapour with nitrous oxide. Similar low-pressure-flame experiments to detect the infrared spectrum of magnesium oxide failed for two reasons. Firstly, <sup>1</sup>S Mg barely reacts with N<sub>2</sub>O<sup>4)</sup> and secondly, the tendency to produce clusters strongly increases towards the lighter members of the alkaline earth metal oxides.

In this contribution we report the detection of the high-resolution infrared spectrum of MgO. The production of the monomeric MgO was enhanced by an additional dc-discharge in the reaction vessel. We have observed 15 rovibrational transitions of the fundamental band and 7 transitions of the first hot band of MgO.

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<sup>1)</sup> H. G. Hedderich and C. E. Blom, *J. Chem. Phys.*, **90**, 4660-4663 (1989).

<sup>2)</sup> H. G. Hedderich, C. E. Blom and A. G. Maki, *to be published*.

<sup>3)</sup> H. G. Hedderich and C. E. Blom, *J. Mol. Spectrosc.*, **140**, 103-111 (1990).

<sup>4)</sup> T. Törring and J. Hoelt, *Chem. Phys. Lett.*, **126**, 477-480 (1986).

Yet Another Resonance in  $\text{H}^{13}\text{CNO}$ 

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A strong Coriolis resonance leading to "forbidden" bands in the FIR high resolution spectrum of the  $^{13}\text{C}$ -species of fulminic acid ( $\text{H}^{13}\text{CNO}$ ) was the topic of a recently published paper<sup>1)</sup>.

Upon extending the analysis of this quasilinear molecule into the mid-infrared we again were presented with some unexpected bands. These bands occur in the neighbourhood of the  $(v_3v_4v_5)^l = (100)^0 \leftarrow (000)$  band at  $1238.1\text{cm}^{-1}$  and the  $(004)^0 \leftarrow (003)^1$  band at  $371.5\text{cm}^{-1}$ . As was the case for the Coriolis resonance, the reason for the anomalies is a resonance already known from the parent species and, once again, this resonance turned out to be much stronger than in the parent species<sup>2)3)</sup>.

The resonance is of Fermi type and connects the states  $(004)^0$  and  $(100)^0$ . The mixing is strong enough to transfer about half of the intensity of the  $(100)^0 \leftarrow (000)$  transition to the  $(004)^0 \leftarrow (000)$  transition, which then appears as one of our "forbidden" bands. A crossing of the unperturbed rovibrational levels is suspected to occur between  $J = 30$  and  $J = 40$ .

Our contribution will present the state of the analysis of the resonance and the spectroscopic constants of the relevant vibrational states.

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<sup>1)</sup>B. P. Winnewisser, M. Winnewisser, G. Wagner and J. Preußner, *J. Mol. Spectrosc.*, in press.

<sup>2)</sup>E. L. Ferretti, K. Narahari Rao, *J. Mol. Spectrosc.* 51, 97-106 (1974).

<sup>3)</sup>K. Yamada, B. P. Winnewisser, M. Winnewisser, *J. Mol. Spectrosc.* 56, 449-470 (1975).

PROVEDELLI M., ZINK L.R., DE NATALE P., DI LONARDO G.,  
INGUSCIO M.: M:

High resolution tunable far infrared spectroscopy of hydrogen  
halides

t e r m i s s i o n

Chairman - P. JENSEN

CARLI B.:

High-resolution far-infrared spectroscopy  
(invited)

CAZZOLI G., DORE L.:

Observation of crossing resonances in the hyperfine structure  
of the  $J = 0$  transition of DC  $^{15}\text{N}$

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The spectroscopic molecular database, **HITRAN**, is the standard compilation of absorption parameters that enable the calculation of atmospheric spectral simulations from the microwave through the visible. HITRAN has been periodically improved and released, the current edition<sup>1</sup> appearing in 1986. A new edition is being prepared for release this year and highlights of the edition will be summarized.

One major effort that will be discussed relates to the improvement for the parameters of carbon dioxide. The work combines the most recent high resolution observations of intensities<sup>2</sup> and line positions with the development of the Direct Numerical Diagonalization<sup>3</sup> method. This theoretical technique has been extended to provide band intensities and Herman-Wallis coefficients for the asymmetric as well as symmetric species of CO<sub>2</sub>. The new results will have a significant impact on remote sensing applications and also provide the basis for high temperature compilations.

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1. L.S. Rothman, *et al.*, *Appl. Opt.* 26, 4058 (1987).
  2. J.W.C. Johns and J. Vander Auwera, *J.Mol.Spectrosc.* 140, 71 (1990);  
V. Dana, A. Hamdouni, R.B. Wattson, and L.S. Rothman, *Appl.Opt.* 29 (1990).
  3. R.B. Wattson, A. Newburgh, and L.S. Rothman, "Herman-Wallis Factors for Carbon Dioxide Calculated by Direct Numerical Diagonalization (DND)," presented at the 45<sup>th</sup> Symposium on Molecular Spectroscopy, Ohio State University, Columbus, Ohio (1990).

LF8 BROWN J.M.:

Infrared spectroscopy of free radicals