

New Techniques in Pulsed Molecular Beam Microwave
Fouriertransform (MB-MWFT) Spectroscopy

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Since MB-MWFT spectroscopy has been developed by Balle and Flygare¹ in 1981, this method was improved by several groups and today it is a versatile means for the investigation of molecules and molecular clusters in the gas phase. Latest contributions in this field will be presented:

- The inherently narrow bandwidth (≈ 1 MHz) of the MB-MWFT spectroscopy has been overcome by automatizing the spectrometer. It is possible now to scan a spectral range of 2 GHz within one day.
- With modern broadband microwave components it became possible to build an apparatus which can be used from 2 to 26.5 GHz without changing the electrical setup.
- Quadrature detection and a CYCLOPS phase cycle is well known in NMR spectroscopy. It turned out to be also advantageous in MB-MWFT spectroscopy.
- Mounting the pulsed nozzle in such a way that the molecular beam propagates along an axis pointing through the center points of both mirrors significantly improved resolution and sensitivity of the spectrometer. Its typical line width is now 2 kHz (FWHM) at 10 GHz, and the accuracy is better than 500 Hz. Such a high resolution is essential if narrow hyperfine patterns (e.g. in $(D_2O)_2$) are to be analyzed, and it turned out to be very useful if centrifugal distortion constants are to be determined if only low-J transitions are available.
- Electric discharges within the nozzle orifice allow to produce molecular species which are difficult to study in static gases. It was possible to observe rotational transitions at vibrational energy levels as high as 6000 cm^{-1} . The discharge in a sulfur dioxide/argon mixture was also used to observe rotational transitions of the SO radical.
- Some new Van-der-Waals complexes (fluorobenzene-argon, 1,2-difluorobenzene-argon, 1,2,3,5-tetrafluorobenzene-argon) studied recently will be presented.

¹ T.J.Balle and W.H.Flygare, Rev. Sci. Instr. 52, 33 (1981).

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Fourier Transform Microwave Spectroscopy of Unstable Molecules
and Their Complexes

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MICROWAVE FOURIER TRANSFORM SPECTRA OF THE Ar-CO, Ne-CO,
AND Kr-CO COMPLEXES

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Pulsed beam microwave Fourier transform spectra of the van der Waals complexes Ar-CO, Ne-CO, and Kr-CO have been studied for four, six, and twelve isotopomers, respectively. They are made up from $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}$, $^{12}\text{C}^{18}\text{O}$; and ^{40}Ar ; ^{20}Ne , ^{22}Ne ; ^{80}Kr , ^{82}Kr , ^{83}Kr , ^{84}Kr , and ^{86}Kr . The ^{17}O nuclear quadrupole hyperfine splittings have been analyzed for the rare gas- $^{13}\text{C}^{17}\text{O}$ species. The rotational and nuclear quadrupole coupling constants are consistent with a structure which is approximately T-shaped, with the O atom slightly closer to the rare gas atom. The effective angles between CO and the a-inertial axis have been estimated from the ^{17}O nuclear quadrupole coupling constants.

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Simple models for properties of hydrogen-bonded and other weak complexes

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The number of hydrogen-bonded complexes characterised by high-resolution spectroscopy is now well in excess of a hundred and rising. In this contribution a review will be presented of the broad generalisations that have emerged from the experimental and theoretical study of hydrogen-bonded and other weak complexes. Very simple physical pictures furnished by the long-range model of intermolecular forces can be used to rationalise isomer preferences and predict semi-quantitatively the angular geometries, dipole moments, electric field gradients at nuclei and spectral intensities. The key role of a distributed representation of the molecular charge distribution will be illustrated. The occasional failures of the crude electrostatic model can also prove instructive.

New results will be presented from a combined experimental/theoretical approach to a value for the nitrogen quadrupole coupling constant in dinitrogen. By considering electrical and motional effects in a series of weak complexes $N \equiv N \cdots HX$ ($HX = HCCH, HCN, HF, HCl, \dots$) it is possible to provide a pseudo-experimental value of $\chi(^{14}N \text{ in free } N_2)$ with error bars that bracket the latest directly calculated values.

In dynamical studies, models of this kind are sufficiently cheap to be useful for preliminary scanning of potential surfaces and estimation of bending potentials before embarking on costly *ab initio* computation at large numbers of geometries for vibrational averaging. This will be illustrated by some work in progress on $NH_3 \cdots HCl$.

The ν_1 Band of $(\text{NO})_2$

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Nitric oxide is well known to exist in the form of dimers, both in the condensed and gaseous phases. The first high resolution spectroscopic detection of $(\text{NO})_2$ was made [1] using MBER to observe 3 rotational transitions in the rf and microwave regions; another line was later measured [2] using the FT microwave technique. Recently, high resolution IR data become available from a pulsed jet/tunable IR diode laser experiment [3], which measured 112 lines of ν_1 with $J \leq 12$ and $K_a \leq 5$, and found a predissociation-limited linewidth of about 200 MHz. In contrast, lines of ν_5 were found to have much larger widths of 4 to 8 GHz. There have also been many photodissociation measurements on $(\text{NO})_2$, most recently an examination [4] of the $\nu_1 + \nu_5$ and $2\nu_5$ dimer bands in the 3600 cm^{-1} overtone region.

In the present work the ν_1 band of the NO dimer was studied using a long-path (84 m) low-temperature (83.5 K) gas cell and a Bomem FTIR spectrometer. Over 440 lines of $(\text{NO})_2$ were measured in the 1840 to 1900 cm^{-1} region, with a resolution of 0.008 cm^{-1} , and assigned to perpendicular transitions with J - and K_a - values up to 35 and 16, respectively. The measurements were analyzed using an s-reduced asymmetric rotor Hamiltonian in order to obtain accurate rotational and quartic centrifugal distortion parameters for $(\text{NO})_2$ in its ground and $\nu_1 = 1$ vibrational states. In this experiment, the NO dimer behaves as a normal semirigid molecule, with no observed perturbations, modest centrifugal distortion effects, and only small changes in parameters due to vibrational excitation. The observed line intensities were used to estimate a value for the dissociation energy of the dimer of $D_0 = 637 \pm 35 \text{ cm}^{-1}$, where the indicated uncertainty depends mostly on an assumption that the vibrational transition moment of NO changes by 40% or less upon complex formation.

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[1] C.M. Western, P.R.R. Langridge-Smith, B.J. Howard, and S.E. Novick, *Mol. Phys.* **44**, 145 (1981).

[2] S.G. Kukolich, *J. Mol. Spectrosc.* **98**, 80 (1983).

[3] Y. Matsumoto, Y. Ohshima, and M. Takami, *J. Chem. Phys.* **92**, 937 (1990).

[4] J.R. Hetzler, M.P. Casassa, and D.S. King, *J. Phys. Chem.* **95**, 8086 (1991).

INFRARED DIODE LASER SPECTRUM OF THE ν_{11} BAND OF N_2O_4 .

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The jet-cooled spectrum of the ν_{11} (b_{3u}) fundamental band of N_2O_4 (antisymmetric combination of symmetric NO_2 N-O stretches) at 1261 cm^{-1} has been measured using a diode laser spectrometer together with a cw-expansion through a slit-shaped-nozzle. Two diodes were used, allowing a rather complete (90 %) coverage of the band. Laser current is swept at a 1 kHz rate, and 100 sweeps are real-time baseline subtracted and averaged for each 0.15 cm^{-1} wide spectral window, allowing a typical signal to noise ratio of 200. The resolution is better than 40 MHz, limited by the free-running laser frequency jitter. N_2O frequencies were used for calibration.

Transitions up to $J=26$, $K_a=12$ have been observed, implying a beam rotational temperature of $\approx 25\text{ K}$. Up to now, 120 ground state combination differences have been fit with a standard deviation of 0.00036 cm^{-1} . From the calculated rotational constants we derive an N-N bond length of 1.75_3 \AA , and NO_2 substructure nearly identical to that of free NO_2 . Spin statistics and a negligible inertial defect verify the identity of the species and establish a planar D_{2h} structure for the ground state. As for the upper state, a perturbation in the $K_a \geq 4$ sublevels is apparent. Using 250 relatively unperturbed lines, the upper state has been fit with a Watson-type asymmetric-rotor hamiltonian to a 0.00043 cm^{-1} standard deviation.