

INFRARED SPECTROSCOPY OF OPEN SHELL MOLECULES

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The spectra of free radicals in the mid-infrared can be detected with great sensitivity by the technique of Laser Magnetic Resonance (LMR). Two laser systems are used in these experiments, the carbon monoxide laser covering the region 1250 to 2025 cm^{-1} (and 2450 to 3500 cm^{-1} with $\Delta v = 2$) and the carbon dioxide laser which operates between 850 and 1100 cm^{-1} . Recent results obtained by this technique will be reported. These will include the observation of species in an electric discharge through methane near 2900 cm^{-1} , the detection of vibration-rotation lines in the spectrum of FeH in its ground and first excited states and the observation of the CCN radical.

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Spectroscopic Studies of Reactive Intermediates

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Rotationally Resolved
Spectr. of Molec. Ions
by ZEKE Photoelectron Spectroscopy.

Sub-Doppler Laser Spectroscopy of Molecules and Clusters

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Summary

This paper gives some examples of Sub-Doppler Laser Spectroscopy of small molecules in the near-infrared, visible and UV-region. With single mode tunable diode lasers around 850 nm and with colour center lasers in the range 1.4 – 1.7 μm vibrational overtone spectroscopy of several hydrocarbon and halogenated hydrocarbon molecules has been performed. In combination with Doppler-free polarization spectroscopy finer details of the spectra could be resolved which lead to a better understanding of anharmonicity effects and vibrational couplings. Electronic transition of CS_2 molecules in a collimated cold molecular beam have been measured with a frequency doubled dye laser in order to investigate the Renner Teller-couplings in the upper state and the spin-orbit interaction between singlet- and triplet states.

Finally some results about sub-Doppler spectroscopy and optical-double resonance experiments on small metal clusters, such as Na_3 are reported.

CONTACT TRANSFORMATIONS OF DIPOLE MOMENT OPERATOR AND RELATED PROBLEMS

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Contact transformations possess one to establish formulas relating effective dipole moment parameters with force field constants and dipole moment derivatives. These formulas can be used for refinement of these molecular constants or for the verification of the consistency of the effective dipole moment parameters and molecular constants when the latter are well known. To have good extrapolation properties of the effective dipole moment parameters in the line intensity calculations this consistency is very desirable.

Three problems have been considered in this work: vibrational dependence of vibrational transition moments for CO_2 molecule, quadratic Herman-Wallis factors for tetrahedral XY_4 molecules and effective Stark Hamiltonian.

Comparison of calculated and fitted values of parameters which are responsible for vibrational dependence of vibrational transition moments of CO_2 molecule gives reasonable agreement for all considered parameters except for one of them. The reasons for this disagreement are discussed.

To compare calculated and fitted values of quadratic Herman-Wallis factors for tetrahedral XY_4 molecules one has to match calculated and fitted sets of effective Hamiltonian parameters by unitary transformation and then to apply this transformation to the effective dipole moment operator. After this kind of transformations we have obtained good agreement between calculated and fitted sets of quadratic Herman-Wallis factors for fundamental bands of methane.

It has been shown that Stark Hamiltonian can be transformed to the effective one which is diagonal relative to the vibrational polyads.