

ROTATIONALLY RESOLVED VIBRATIONAL OVERTONE SPECTRA OF
JET-COOLED METHANOL

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Interpreting the spectral structure of high vibrational overtone transitions in terms of the dynamics of the excited molecules requires spectral simplification to remove inhomogeneous broadening. Infrared-optical double resonance excitation permits the measurement of fully rotationally resolved vibrational overtone spectra of jet cooled methanol up to the $6n_{\text{OH}}$ level. These weak transitions to high vibrational levels are detected using the technique of infrared laser assisted photofragment spectroscopy (IRLAPS).

This involves selectively dissociating the vibrationally excited molecules *via* infrared multiphoton excitation using a CO₂ TEA laser and then spectroscopically detect the resulting decomposition products using laser induced fluorescence. Scanning the overtone excitation laser frequency while keeping all others fixed generates an overtone excitation spectrum of the jet-cooled molecules. Such spectra carry detailed information on the intramolecular dynamics of the highly excited molecules. The elimination of spectral congestion reveals splittings of the zeroth-order rovibrational levels that reflect vibrational coupling to dark background levels. Analysis of the overtone spectra as a function of number of OH stretch quanta indicate the presence of a strong coupling between zeroth-order states with n_{OH} and those with $(n-1)n_{\text{OH}} + 1n_{\text{CH}}$ (asym. st.) This coupling is most clearly manifest at the $5n_{\text{OH}}$ level where the OH stretch frequency is anharmonically shifted close to that of the CH asymmetric stretch frequency. Finer spectral splittings in the spectrum reflect the coupling of the mixed OH-CH stretch states with the rest of the vibrational bath. The most recent results using this technique for CH₃OH and its partially deuterated analogs will be discussed.

THEORETICAL STUDY OF VIBRATIONAL OVERTONE SPECTROSCOPY
AND DYNAMICS IN METHANOL

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Experimentally observed coupling^a between OH and CH stretching modes in the high overtone region has been modelled successfully in terms of a curvilinear internal coordinate Hamiltonian including harmonic coupling between anharmonic OH and CH stretching oscillators and cubic Fermi resonance kinetic and potential energy couplings between CH stretches and HCH bends. The Hamiltonian matrices have been setup in block diagonal forms including only resonant states. The potential energy parameters have been optimised by the least squares method using experimental vibrational term values as data. The OH/CH stretch interaction parameter obtained agrees well with the one calculated by perturbation theory from a published *ab initio* harmonic force field. The model has reproduced well experimental band origins in the OH stretching overtone region and it has provided assignments for the bending overtones in the CH stretching fundamental region. Finally, a unitary transformation is found from the internal coordinate representation to the corresponding normal coordinate representation providing a set of normal coordinate parameters like diagonal anharmonicity parameters, Darling-Dennison resonance constants and cubic Fermi resonance force constants. Our results confirm the experimental finding of energy redistribution between the OH and CH stretching modes on 100 fs time scale in the case of $5\nu_{\text{OH}}$.

^aL. Lubich, O. V. Boyarkin, R.D.F. Settle, D.S. Perry, and T.R. Rizzo, Faraday Discuss. Chem. Soc. (in press).

LABORATORY DETECTION OF PROTONATED FORMALDEHYDE (H_2COH^+) IN RANGE OF C=O STRETCH

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A recent analysis of the rotational-vibrational spectrum H_2COH^+ was based on the measurement of Amano and Warner [1]. Their first spectroscopic identification has been made by observing the ν_1 fundamental band (O-H stretch) in 2.9 μm region with difference frequency laser system.

We have now extended this study by using of diode lasers measurement in the region 1670-1750 cm^{-1} with Doppler limited resolution at 270 K. We used a diode lasers manufactured by Aero Lasers, mounted in a conventional cold head. The laser beam made 28 traversals of a 1m long hollow cathode. H_2COH^+ absorption was detected by amplitude (on-off) discharge modulation [2], followed by phase sensitive demodulation of transmitted signal at 2f. Protonated formaldehyde was generated by discharging a mixture of H_2 (1 Torr) and H_2CO (20 mTorr) which was obtained by heating paraformaldehyde powder. The cathode was cooled to 0°C by circulating cooled water and ethanol. Wave number calibration was made by means of simultaneous recording of signals from an absorption cell containing NH_3 [3], and solid stabilized Ge etalon.

Over 100 P- and R- branch transitions of different K have been measured, assigned and fitted by diagonalizing a standard asymmetric-top Hamiltonian in the A-reduced representation [4].

- [1] T. Amano and H. E. Warner, *Astrophys. J.* **342**, L99 (1989).
- [2] Z. Zelinger, S. Civiš, P. Kubát, and P. Engst, *Infrared Phys. Technol.* **36**, 537 (1995).
- [3] G. Guelachvili and K. Narahari Rao, *Handbook of infrared standards* (Academic Press, New York, 1986).
- [4] J.K.G Watson, in *Vibrational Spectra and Structure*, Vol. 5, ed. J.R. During (Amsterdam, Elsevier).

MEASUREMENTS OF THERMOSPHERIC COOLING PROCESSES
FROM A TETHERED SATELLITE PLATFORM

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The major thermospheric cooling processes are the collisional production of vibrationally excited states of CO_2 and NO and the excited fine structure states of atomic oxygen, followed by radiation. Tethered probes offer a unique opportunity for studying the lower thermosphere, through a combination of remote-sensing and *in situ* measurements, thus enabling significant progress in the overall understanding of the energy budget in this region. An instrumentation package, with excellent technical heritage, which includes a neutral mass spectrometer and a limb-observing infrared spectrometer, can make comprehensive and definitive measurements of these important, but as yet poorly-quantified, cooling processes. This talk briefly reviews the scientific issues in upper atmospheric radiative cooling and describes a candidate system for carrying out the necessary measurements.

QUANTUM-MECHANICAL STUDIES OF RADIATIVE
ASSOCIATION REACTIONS: THE FORMATION OF HeH^+ , NeH^+
AND ArH^+

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Radiative association processes play an important role in the formation of interstellar molecules by gas phase ion-molecule reactions. Due to experimental difficulties, only a few radiative association reactions have been studied in the laboratory. Therefore most processes of interstellar importance must have their rates obtained by theoretical methods. Especially statistical approaches were successfully applied in the past to predict the association rates of larger molecular complexes. A complete understanding, however, of the different possible reaction mechanisms can only be deduced from detailed quantum-mechanical treatments. Such rigorous *ab initio* calculations of the radiative association formation of noble gas hydride ions XH^+ ($X=\text{He, Ne, Ar}$) are described here to discuss the requirements and limitations of this approach. Rate coefficients of all possible radiative association reactions resulting from $X + \text{H}^+$ and from $X^+ + \text{H}$ collisions are calculated over a wide temperature range. For this purpose the potential energy and electric dipole moment functions of the corresponding $\tilde{X}^1\Sigma^+$ ground electronic and the first excited $\tilde{a}^3\Sigma^+$ and $\tilde{A}^1\Sigma^+$ states are determined at the configuration interaction level of theory and the electronic transition dipole moment functions between the two $^1\Sigma^+$ states are evaluated using the state interaction method of Malmqvist and Roos. From the potential energy functions, all rotation-vibration bound and rotationally quasi-bound levels are obtained for each electronic state. In the present diatomic systems the only efficient formation occurs in the two-state process $X^+ + \text{H} = \text{XH}^+ (\tilde{A}^1\Sigma^+)^* \rightarrow \text{XH}^+ (\tilde{X}^1\Sigma^+) + h\nu$ in which radiative stabilization is achieved through transition from the initial quasi-bound levels of the excited $\tilde{A}^1\Sigma^+$ state to the bound rotation-vibration levels of the ground electronic state. The temperature dependence of the corresponding rate coefficients show the typical behavior with a maximum at low temperatures and a rapid fall-off when temperatures rise above 100 K. In case of the HeH^+ system, potential functions obtained from previous highly accurate directly correlated wavefunction calculations are used to assess the reliability of the present results.

HYPERFINE STRUCTURE OF ROTATION-INVERSION LEVELS IN THE EXCITED ν_2 STATE OF AMMONIA

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Rotation-inversion transitions with $J = 3 \leftarrow 2$, $s \leftarrow a$, and $K = 0, 1, 2$, and with $J = 0 \leftarrow 1$, $a \leftarrow s$, and $K = 0$ in the excited ν_2 vibrational state have been measured by Lamb-dip saturation spectroscopy using the Cologne terahertz spectrometer with an accuracy about 5kHz. The line frequencies of hyperfine structures of the rotation inversion transitions have been simultaneously analyzed (together with a previously published ν_2 transition $J = 2 \leftarrow 1$, $s \leftarrow a$, $K = 1$, see Hüttner W. and Majer W., Mol. Phys. **52**, 631 - 636 (1984)) in terms of effective nuclear quadrupole and spin-rotation parameters for both the inversional states. The hyperfine parameters have been determined including effective centrifugal distortion effects. In addition to these, unperturbed rotation-inversion energy levels have been obtained with a kHz precision. The calculated results are compared with a previous theoretical predictions. The possible effects of the hydrogen spin interactions will be also discussed.

The results obtained in the presented study are also used to the analyses of transition profiles to improve the precessions of pure inversion, rotation-inversion, and vibration-rotation frequencies removing the hyperfine distortion effects.