

ABSOLUTE INTENSITY MEASUREMENTS ON THE VIBRATION-ROTATION TRANSITIONS OF AMMONIA

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The vibration-rotation spectrum of ammonia in the 10 μm region, the fundamental inversion band ν_2 , was recorded with high resolution and high precision using a Bruker IFS-120 HR spectrometer at Nobeyama Radio Observatory. In order to secure the accuracy in the intensity measurement, the experiment was carried out in room temperature (25°C) with the following conditions.

1. The spectra were recorded with the highest resolution (0.002 cm^{-1}) available.
2. The interferogram was converted by FFT without any apodization (boxcar apodization).
3. Sample pressure of 15 Torr was applied for broadening the lines in order to obtain enough number of measured points for each line.
4. A short cell of 374 mm path length was used to keep the peak absorption not too large for many lines.

The recorded line profiles were analyzed assuming the Voigt-type line shape. The intensity parameters, the pressure broadening parameters, and the line positions were adjusted by a least-squares fit procedure to reproduce the experimental line profiles for some selected lines. The effective transition dipole moment for each line was derived from the obtained line intensities. It is clearly seen that the observed line intensities deviate significantly from the rigid rotor approximation. The Herman-Wallis factors have been determined as listed in Table 1, using the formula derived for symmetric rotors by Watson.

Table 1
Vibrational Transition Moment and Herman-Wallis Factors
of NH_3 for the ν_2 Band

Parameter	$a \leftarrow s$	$s \leftarrow a$	Unit
μ_2	0.236 3(22)	0.247 3(10)	D
A_2^J	0.001 28(70)	-0.000 58(28)	none
$A_2^{JJ(Q)}$	-0.000 55(10)	-0.000 674(55)	none
$A_2^{JJ(PR)}$	-0.000 49(13)	-0.000 798(58)	none
A_2^{KK}	0.000 72(10)	0.000 903(47)	none

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LIFETIMES OF THE LOWEST TRIPLET STATES 3A_2 AND 3B_2 OF OZONE BY INTRACAVITY LASER ABSORPTION SPECTROSCOPY

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High resolution spectra (0.012 cm^{-1}) of the highly structured first members of the Wulf progression in the near infrared spectral range at around $1\text{ }\mu\text{m}$ ($9100\text{--}10520\text{ cm}^{-1}$) have been measured using two recently developed all solid state Ti:sapphire and Nd:glass intracavity laser absorption spectrometers. An analysis of the rotational structure confirmed the 3A_2 and the 3B_2 states to be the upper states in most of these transitions, which are the lowest excited (triplet) states in ozone. In this contribution we will focus on the lifetimes of the excited states (from linewidth measurements of the corresponding transitions from the ground state) which, unexpectedly, have been found to depend upon the J rotational quantum number, as well as K, and vibrational excitation. The short lifetimes inferred from these linewidths suggest that none of these triplet states is metastable nor long lived. The interesting state resolved intra- and unimolecular dynamics of this molecule after photoexcitation in the near infrared, which have been inferred from the spectral features and perturbations of the high resolution spectra, will be compared with theory, e.g., predictions of the dynamics on calculated potential energy surfaces. The impact of the results on the recombination kinetics, heavy isotope enrichment, photochemistry, and the atmospheric chemistry of this molecule is discussed.

RADIATIVE DISSOCIATION AND PREDISSOCIATION OF HeH RYDBERG STATES

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The repulsive ground electronic state $\tilde{X}^2\Sigma^+$ of HeH is strongly coupled at small internuclear distances to the low-lying Rydberg states and similar couplings also exist between some of the Rydberg states themselves. The capture of low-energy electrons by HeH⁺ ions in a Rydberg state leads to the formation of helium ground state atoms and of hydrogen either in the ground or excited electronic states by indirect predissociation. In the present contribution highly accurate *ab initio* spectroscopic data for the lowest electronic states correlating on dissociation with the H(*ns*) asymptote with $n=1,2,3$ are presented. Coupling matrix elements between these states are calculated in order to determine individual transition rates as well as total radiative and non-radiative life times for the lower vibrational and rotational levels.

INTERACTING HIGHLY EXCITED ROTATIONAL LEVELS OF WATER

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In an attempt to understand the rotational energy level pattern of the water molecule for high K_a -values, emission spectra of methane-oxygen low-pressure flames have been used to retrieve rotational energies for an extended set of vibrational states belonging to this molecule. In this talk only the results relevant to the ground and (010) vibrational states will be presented. Experimental energies, along with their uncertainties, were derived up to $J = K_a = 25$ for the former state and up to $J = K_a = 21$ for the latter. These new values of the rotational energies have been fitted using the theoretical treatment developed to account for anomalous centrifugal distortion effects.^a Although the present data set includes rotational levels characterized by much higher K_a -values than those considered in a previous analysis,^a it has been possible to satisfactorily reproduce the experimental energies for the two lowest vibrational states, and this provided a check for the accuracy of the observed rotational energies. This analysis also revealed strong accidental resonances between rotational levels of the (010) state and those of the first triad. Unlike the strong accidental resonances already evidenced in the water molecule,^b these resonances occur between two different polyads. These new results will be discussed in the paper and we will try to understand why the theoretical model^a used for the analysis of the ground and (010) states may need to be altered when applied to fitting a larger set of rotational levels.

^aL. H. Coudert, *J. Molec. Spectrosc.* **181**, 246 (1997).

^bC. Camy-Peyret and J.-M. Flaud, *J. Molec. Spectrosc.* **59**, 327 (1976).

State selective predissociation spectroscopy of HX^+ ($\text{X}=\text{Cl}, \text{Br}$) ions

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The state selective predissociation spectroscopy of the hydrogen chloride (HCl^+) and the hydrogen bromide (HBr^+) ion has been investigated in a two color laser experiment. Here the first laser serves for the formation of ions with a rather narrow but tunable rotational state distribution (preselection) via a 2+1 REMPI transition. The second laser induces the predissociation via the $^2\Sigma^+(v') \leftarrow ^2\Pi_i(i=1/2, 3/2, v''=0)$ transition. The predissociation (PD) is in each case detected via detection of the fragment ion (Cl^+ or Br^+).

In this experiment it is demonstrated that the state selective photodissociation of these ions is possible with complete control of the rotational and spin angular momentum as well as the parity for some of the $^2\Sigma^+(v')$ states. This experiment allows to determine rotationally state selected dissociation thresholds. For example in the $^2\Sigma^+(v'=1)$ state of the HBr^+ ion 12 rotational quanta with the spin parallel to the rotational angular momentum ($R'=12, J'=12.5$) are required for the dissociation [1]. The state with $R'=12$ but the spin antiparallel to the rotational angular momentum ($J'=11.5$) does not dissociate.

From the rotationally resolved PD spectra the corresponding state selective lifetimes can be deduced. With increasing vibrational quantum number this lifetime decreases considerably. Our experimentally determined lifetimes cover a range from about 20 ps down to about 10 fs.

In the experiment discussed above the first laser provides a preselection of ions regarding their rotational state distribution, employed for the state selective photodissociation in the second step. However, the state selective predissociation in the 2nd step can also be viewed as a very sensitive probe for unexpected parity transitions in the formation of the ions. This allows conclusions regarding the orbital angular momentum composition of the Rydberg states employed in the REMPI process.

[1] M. Penno, A. Holzwarth und K.-M. Weitzel, J. Phys. Chem. A, 102, 1927, (1998)

LASER INDUCED EMISSION SPECTROSCOPY OF CARBON MOLECULES IN SOLID ARGON

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Carbon molecules were discovered in stellar atmospheres, in cometary tails and play also an essential role in formation of fullerenes and nanotubes. Whereas the properties of small species up to C_3 and of several fullerenes are well known, our knowledge about the middle-sized clusters is very limited. To contribute to spectroscopic characterization of the carbon molecules, we studied their fluorescence and phosphorescence emission spectra. Our laboratory setup combines the matrix isolation technique with high-resolution absorption spectroscopy and laser induced emission spectroscopy. By optimizing the apparatus, we reached an excellent detection sensitivity. At the moment, we can detect emission peaks with equivalent quantum yields of less than 10^{-8} . This success made it possible to observe extremely weak fluorescence spectra of carbon clusters larger than C_3 . The analysis of the spectra yielded the frequencies of the symmetrical stretchings in the electronic ground states of the observed molecules. Till now, we studied emission and excitation spectra of linear C_3 and C_6 . The work on other carbon molecules is in progress.