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Depletion modulation of Ar–H₂O in a supersonic planar plasma

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Abstract

A sensitive detection technique for tunable diode laser spectroscopy is presented that is suited to study rotationally resolved spectra of weakly bound complexes. The method uses a low energetic plasma source to achieve an efficient concentration modulation in a supersonic planar jet expansion. The method is demonstrated with rotationally resolved spectra of the $\Pi(1_{10}) \leftarrow \Sigma(1_{01})$ and $\Pi(2_{12}) \leftarrow \Sigma(1_{01})$ internal rotation/vibration bands of *ortho* Ar–H₂O in the ν_2 bend region of H₂O. The latter transition has not been reported before and is recorded at 1658.0309(6) cm⁻¹. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Phase-sensitive detection schemes, using lock-in amplifiers, are routinely used in spectroscopy to increase the sensitivity of direct absorption experiments. In the case of tunable diode lasers frequency modulation is often used for this purpose: by periodically varying the current of a diode laser fractional changes of the order of 10⁻⁵–10⁻⁶ have been recorded. Unfortunately, such changes are also induced by multipass interferences between optical elements, essentially low Q-cavities which can result in an intensity modulated baseline. This limits the final possible sensitivity of the method; absorption signals get lost in a pattern of étalon fringes, particularly when absorption signals are

weak. The latter is a problem in the study of molecular complexes, typically bound by weak van der Waals forces or hydrogen bridges. In the infrared such species are mainly studied in supersonic slit jet expansions and an effective way to prohibit fringing for example is to combine frequency and concentration modulation [1]. In most jet studies reported so far (see e.g. [2,3] and references therein) *production* modulation has been applied. *Depletion* modulation is expected to be comparably efficient but applications are reported only in the case of Ar–CO and the CO-dimer [4,5]. In the latter experiment a discharge perpendicular to the expansion has been used to break the intermolecular bonds. Here another technique is described which uses electron impact ionization. The method has the advantage that plasma noise can be neglected – as a consequence double modulation schemes are not necessary – and that the rotational cooling in the expansion is hardly

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affected by the plasma. The performance is demonstrated on the example of rotationally resolved and rotationally cold spectra of the molecular complex Ar–H₂O.

2. Experiment

The complexes are formed by passing argon through distilled water at room temperature. The mixture containing several Torr of water vapour in argon is then expanded continuously through a 32 mm × 50 μm long slit into a vacuum chamber. This chamber is evacuated by a 2150 m³/h roots blower system backed by a 120 m³/h rotary pump, providing pressures better than 0.2 mbar during jet operation. The expansion is sampled by the light of an infrared tunable diode laser. Part of the infrared beam is guided through a reference gas cell and an external étalon for calibration purposes, yielding absolute accuracies better than 0.002 cm⁻¹. The main part of the laser beam is guided via a system of mirrors and lenses into the vacuum chamber and multipasses a planar jet using a Perry optical system to increase the total absorption path length to approximately 0.5 m.

Depletion modulation is obtained in the following way (Fig. 1): the expansion is irradiated with electrons that are emitted by a tungsten wire (diameter 0.2 mm) that is strongly heated to ~1500 K by a current of 2–4 A. The filament is mounted in a slotted molybdenum tube that is positioned parallel to and slightly below the slit. The tube is put on the same negative potential as the filament. A slotted stainless steel shield, kept at earth potential, is mounted just above the tube in order to accelerate the electrons towards the jet. The impact of the electrons with the expanding gas initiates a plasma in which the excess energy causes weakly bound complexes to dissociate. The concentration is modulated by switching the plasma on and off very rapidly applying a sinusoidal voltage (peak-to-peak voltage of 0/–150 V) to filament and molybdenum tube. The maximum modulation frequency is about 15 kHz and depends on the time molecules need to cross the absorption zone. Noise caused by the background emission of the plasma is low and is

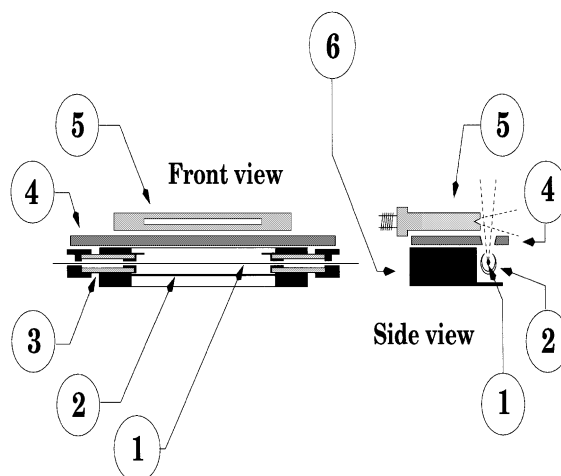


Fig. 1. A schematic view of the slit nozzle device. A heated tungsten filament (1) mounted inside a slotted molybdenum tube (2) via ceramic insulators (3) emits electrons via a slotted stainless steel shield (4) towards gas that is expanded through a 32 mm × 50 μm slit (5). The filament unit is mounted on a copper block (6) that is water cooled. The copper block is attached to a translation stage that varies the distance between filament and nozzle orifice.

further reduced by an infrared bandpass filter in front of the detector. The signals are recorded phase sensitively using a lock-in amplifier. The phase of the absorption provides additional information on the origin of the signal; species depleted or formed (e.g. ions) in the expansion absorb 180° out of phase.

3. Results

In Fig. 2 the Q-branch range is shown of the $\Pi(1_{01}) \leftarrow \Sigma(1_{01})$ vibrational band of *ortho* Ar–H₂O upon excitation of the ν_2 bending of water. This band has been studied in detail before [6] which allows a straightforward assignment. Clearly, S/N ratios are good and line widths are of the order of 100 MHz. The latter are limited by instrumental noise, such as frequency noise and residual Doppler broadening in the multipass system. No serious loss in rotational cooling is observed as due to the plasma. The upper trace in the graph of Fig. 3 shows the Boltzmann plot for the Q-branch transitions of this band; the rota-

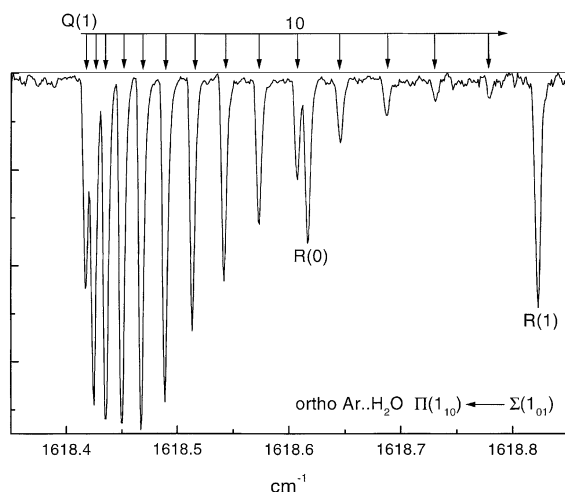


Fig. 2. The $\Pi(1_{10}) \leftarrow \Sigma(1_{01})$ band of *ortho* Ar–H₂O upon bending excitation of the H₂O unit, using depletion modulation in a planar plasma expansion.

tional temperature is determined as $T_{\text{rot}} = 6.0(5)$ K which is similar to the value found previously in a pulsed planar expansion *without* plasma modulation [6]. The plasma does not influence the cooling in the slit expansion.

A red shaded band system with similar characteristics but not reported in the literature so far is located around 1658 cm^{-1} , shifted approxi-

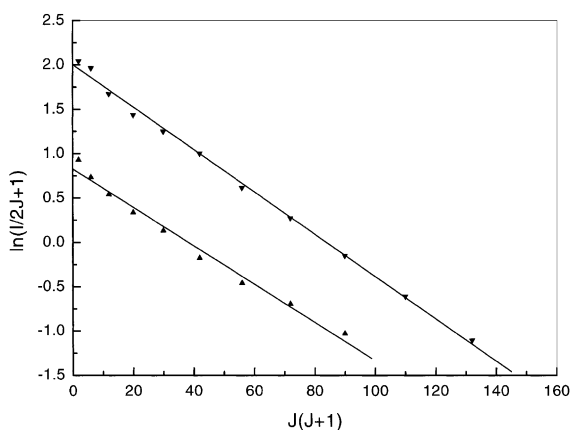


Fig. 3. A Boltzmann plot for the Q-branch transitions shown in Fig. 2 (upper trace) and Fig. 4 (lower trace). In both cases rotational temperatures $T_{\text{rot}} \approx 6$ K are found. This indicates that the rotational cooling in the expansion is hardly affected by the plasma.

mately 40 cm^{-1} to higher energy of the $\Pi(1_{10}) \leftarrow \Sigma(1_{01})$ band. The Q-branch range as well as the lowest rotational transitions are shown in Fig. 4. The Boltzmann plot is shown in the lower trace of Fig. 3. The measured line positions are listed in Table 1. High resolution ground state combination differences with the observed far infrared [7,8] and infrared bands [6,9] make an assignment to a transition starting from the $\Sigma(1_{01})$ state of *ortho* Ar–H₂O unambiguous. The *vibrational* assignment becomes possible from the band profile that is typical for a Π – Σ transition and by combining all known transition frequencies of the free monomer and the Ar–H₂O complex. The band system observed here is approximately 63 cm^{-1} above the frequency found for the ν_2 bending of the free H₂O monomer at $1594.7449(88) \text{ cm}^{-1}$ [10]. This value is close to the 61.4 cm^{-1} splitting found between the $\Pi(2_{12})$ and the $\Sigma(1_{01})$ levels in the vibrational ground state. Upon ν_2 excitation of the free H₂O monomer the $2_{12}-0_{00}$ energy separation increases from 79.50 cm^{-1} in the ground state to 82.32 cm^{-1} in the excited state [10]. In a free rotor limit the difference of 2.82 cm^{-1} adds to the observed far infrared value of 61.4 cm^{-1} as both transitions start from the same $\Sigma(1_{01})$ level. As a consequence, the $\Pi(2_{12})$ origin is expected around 1659.0 cm^{-1} , only 1 cm^{-1} to the blue of the band system observed here. An assignment to the $\Pi(2_{12}) \leftarrow \Sigma(1_{01})$ transition, therefore, is obvious.

The *rotational* analysis of the observed transitions has been performed, taking into account that the (e, f) symmetry degeneracy of the Π energy levels is removed due to Coriolis interactions (see also [6]). In a simple and practical approximation this splitting can be described in terms of the l-doubling parameter q . The observed frequencies are fitted to the pseudodiatomic energy level expressions

$$E_{P,R}(J) = \nu_{\Pi} + B'[m(m+1) - 1] - D'[m(m+1) - 1]^2 + \frac{q}{2}m(m+1) - [B''m(m-1) - D''m^2(m-1)^2]$$

with $m = -J$ for P-branch and $m = J + 1$ for R-branch transitions and

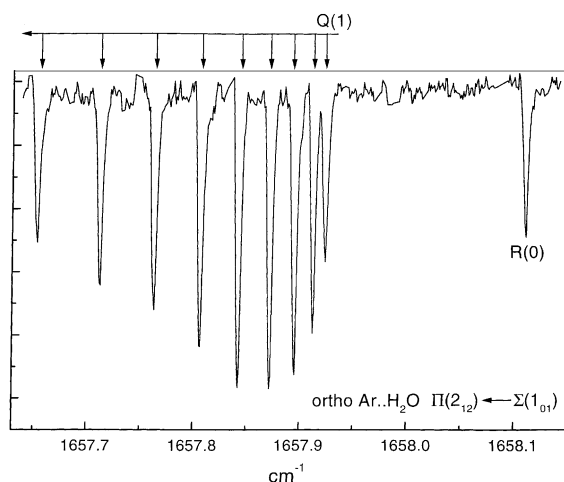


Fig. 4. The $\Pi(2_{12}) \leftarrow \Sigma(1_{01})$ band of *ortho* Ar–H₂O upon bending excitation of the H₂O unit, using depletion modulation in a planar plasma expansion.

Table 1
Observed line positions for the $\Pi(2_{12}) \leftarrow \Sigma(1_{01})$ band of *ortho* Ar–H₂O

Transition	ν (cm ⁻¹)	$o - c^a$
P4	1657.1410	-11
P3	1657.3463	16
P2	1657.5448	2
Q1	1657.9300	-3
Q2	1657.9188	-2
Q3	1657.9014	-5
Q4	1657.8779	-11
Q5	1657.8489	-12
Q6	1657.8140	-10
Q7	1657.7729	-5
Q8	1657.7249	-2
Q9	1657.6709	11
Q10	1657.6086	15
Q11	1657.5377	12
Q12	1657.4561	-17
R0	1658.1286	13
R1	1658.3179	20
R2	1658.5005	-9

^a In units of 10⁻⁴ cm⁻¹.

$$E_Q(J) = \nu_{\Pi} + B'[J(J+1) - 1] - D'[J(J+1) - 1]^2 - \frac{q}{2}J(J+1) - [B''J(J+1) - D''J^2(J+1)^2]$$

for Q-branch transitions. When the ground state parameters are kept fixed to the available microwave values [11], this gives: $\nu_{\Pi} = 1658.0309(6)$ cm⁻¹, $B' = 0.095026(54)$ cm⁻¹, $D' = 3.7(5) \times 10^{-6}$ cm⁻¹ and $q = 1.4(1) \times 10^{-3}$ cm⁻¹. The resulting observed minus calculated ($o - c$) values are below the experimental uncertainty (Table 1).

The l-doubling parameter q is related to the Coriolis interaction term β and the energy difference $\Delta\nu$ between the interacting states via $q = \beta^2/(\Delta\nu)$ [12]. In the case of a state with $j = 1$ the value of β is approximately $2B$. A fit of the transitions of the $\Pi(1_{10}) \leftarrow \Sigma(1_{01})$ band observed here and listed in [6] results in $q = 2.24(3) \times 10^{-3}$ cm⁻¹, indicating that a state with $\Sigma(1_{10})$ symmetry located around 1634 cm⁻¹ (i.e. $\Delta\nu \approx 16$ cm⁻¹ [6]) is the primary interacting state. In the case of the 2_{12} states mixing is more complex, as has been discussed in detail in [7]. The q -value derived here for the $\Pi(2_{12}) \leftarrow \Sigma(1_{01})$ band confirms this. The calculated $\Delta\nu$ value is too large to be due to a mixing with the close lying $\Sigma(1_{12})$ state only [13] and interactions with other states are very likely. At this stage, however, it is not possible to characterise the mixing in more detail, as many of the possible perturbing states have not been identified yet.

The present method will be generally applicable for other weakly bond complexes. The dissociation energy of Ar–H₂O is 127(5) cm⁻¹ [14]. Complexes less strongly bond will be principally accessible by this method, but it is expected that the plasma energy is sufficiently large to dissociate complexes with considerably stronger bonds as well.

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