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Tunable infrared and far-infrared direct absorption spectroscopy of molecular ions in a supersonic jet expansion

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Abstract

A newly designed two-dimensional corona-excited slit nozzle discharge is described and its first applications for direct absorption spectroscopy of molecular ions in a supersonic expansion in the infrared (NO^+) and far-infrared (N_2H^+). The results are discussed and it will be shown that under the conditions described, for N_2H^+ linewidths of 750 kHz and rotational temperatures of 12 K can be achieved.

1. Introduction

Direct absorption spectroscopy of ions in the far-infrared is usually performed with the use of hollow cathode or magnetically extended negative glow discharges (see e.g. refs. [1,2]). In both cases, the larger part of the discharge consists of a negative glow, which is an ion-rich discharge region. Although these glass tube discharges form effective methods for the production of ions, they have the disadvantage of bad rotational cooling. Even with liquid nitrogen cooling, rotational temperatures are of the order of 100 K. Furthermore, number densities are low, since high pressures will make the discharge unstable and in the far infrared pressure broadening will become a serious problem. As a consequence complex formation will hardly take place. It is for this reason that until now just one ion complex, ArH_3^+ [3,4], was found.

In infrared experiments ions are also generated in normal discharges. In this type of discharge the positive column is observed, where the ion density is lower as in the negative glow region. But normal discharges can be operated at much higher pressures and as long as pressure broadening is negligible, for this disadvantange can be made up. Moreover spectroscopy in the positive column allowed the introduction of velocity modulation, a sensitive ion-selective detection scheme [5] that initiated a great activity in the field of infrared ion spectroscopy. The cooling properties, however, are still poor and although complex formation could take place, due to the higher pressures, no ion complexes have been observed until now. The reason is, that with higher degrees of freedom the number of states increases, which implies that the population density in each state is expected to be too small to be detected. For this reason cooling of ion complexes is highly desirable, since it should restrict the population to the lowest states. This can be achieved by combining expansion and discharge techniques.

In 1983 a realization of a corona-excited supersonic expansion through a circular nozzle was reported by Droege and Engelking [6]. This technique turned out to be an effective way to study radicals with LIF spectroscopy [7], but since the absorption length is small it is not a good alternative to direct

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absorption spectroscopy. Only SH^+ was measured in a free expansion by Hovde and Saykally [8], using a setup similar to the one used by Droege and Engelking in combination with LMR techniques. In this case detection was only possible because the sensitivity of the LMR setup was increased, compared to ordinary absorption spectroscopy. Another way to use expansions for direct absorption ion spectroscopy was reported by Coe et al. [9], using fast ion beams. This complicated technique, that allows for mass selective detection at the same time, looked promising, but the rotational temperatures achieved are still high (420–600 K) [10].

In general the absorption length in a point nozzle expansion is not sufficient. For this reason much work on expansion cooled radicals was performed using (pulsed) slit jets – where absorption lengths are longer – either combining it with excimer laser photolysis [11] or corona excitation [12]. Recently Comer and Foster [12] reported the use of a continuous corona-excited supersonic slit nozzle expansion for the detection of CS and NH_2. Slit nozzles are more difficult to handle, but offer some advantages. The smaller Doppler widths associated with the planar expansion increase resolution and peak intensity. Furthermore the absorption length between molecular and laser beam is increased, yielding larger absorption signals. However, until now these techniques have not been used for the detection of ions.

In this Letter the first direct absorption signals of ions in the infrared and far infrared are presented, with a continuous high-voltage high-pressure slit nozzle discharge. This type of discharge has several advantages compared to the bulk discharges mentioned before:

- small Doppler width, yielding narrow linewidths;
- expansion cooled, yielding low rotational temperatures, which will simplify the analysis of complex spectra; but is also a necessary condition for complex formation;
- a relatively simple setup, with small absorption lengths (typically 5 cm) but high molecular densities.

The slit nozzle discharge has also a major disadvantage in that a stable continuous expansion from a 5 cm × 150 μm slit has to be maintained, which necessitates the use of large pumps (3000–4000 m^3/h). As a consequence the gas consumption is large.

Here we report the first results on rovibrational transitions of NO^+ (see also ref. [13]) and rotational transitions of N_2H^+ using a cw slit nozzle discharge. The nitrosyl ion is assumed to play an important role in atmospherical chemistry [14] and may exist in interstellar space [15]. Until now only six rovibrational transitions in the $X\,^1\Sigma^+$ ground state have been measured in the infrared [16]. From these transitions the band origin could be determined as well as the molecular parameters for the excited vibrational level, using the (sub)millimeter data found by Bowman et al. [17].

N_2H^+ is a well-known linear ion [1,18], that is regarded to be of interstellar interest. In 1990 the electric dipole moment was determined experimentally by Havenith et al. [19]. In this work we present several rotational transitions from which the rotational temperature can be determined. Furthermore it will be shown that with the new technique narrow linewidths for ions can be achieved.

2. Experimental

One of the problems in obtaining a stable discharge in a slit nozzle is to extend the discharge over the whole length of the slit (5 cm). Since a discharge normally will run on a single point – from which the Droege–Engelking discharge benefits – it is necessary to use several independent electrodes that are isolated from each other by resistances (100 kΩ) and that are connected to the same high voltage power supply (Fig. 1). When the discharge does not run at one electrode, there will be no voltage drop over its resistor. The voltage at that specific electrode will become higher than the starting voltage of the discharge and a restart of the discharge at that point will be induced. In this way a quasi-continuous discharge is created over the whole length of the slit. It is important to choose the resistances in such a way that a restart of the discharge at one of the electrodes does not cause a voltage drop at its resistance below the burning value. This value is approximately two times smaller than the starting voltage.

In the experiments described, we have used slit nozzles of 5 cm × 150 μm in which five to seven electrodes are mounted. Typical discharge conditions are 2 kV in front of the resistances, 50–80 mA, backing pressures of about 300 Torr and a pressure of 200

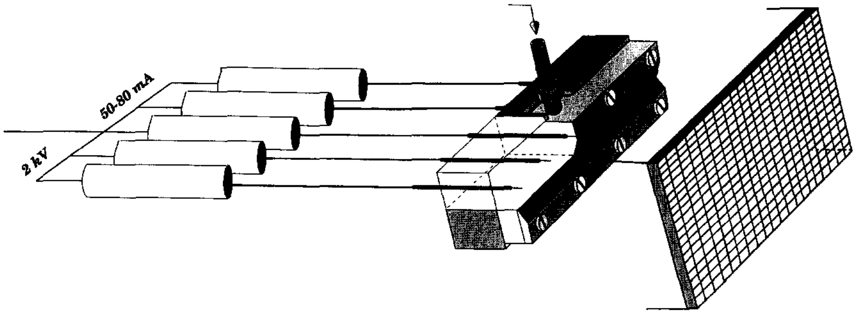

Fig. 1. The setup for the high-voltage high-pressure slit nozzle discharge.

mTorr in the vacuum chamber during jet operation. The voltage across the discharge is typically around 500 V.

In the infrared experiment (Bonn) we have combined the computer-controlled diode laser spectrometer [20] with a crossed molecular jet setup. As was reported by Huber and Vervloet [21] NO^+ can be produced efficiently by diffusing NO on a beam of metastable He. This is expected to be the best way to populate the excited $^3\Sigma$ state, which is the future goal of our setup. In the experiment described here we have used the slit nozzle discharge to produce a stable source of He*. The second slit nozzle ($5\ \text{cm} \times 50\ \mu\text{m}$) – without discharge – is positioned perpendicular to the He* jet, about 1.5 cm from the reaction centre. The infrared beam multipasses the reaction zone four times and the absorption signal can be detected both by frequency modulation, high voltage and double modulation [22]. The best results were obtained using HV modulation.

In the far-infrared setup (Nijmegen) we have used the tunable sideband spectrometer, that was described in detail before [23]. The N_2H^+ ions are generated in the expansion of a gas mixture of N_2 and H_2 flowed in a ratio of approximately 10:1 through the slit nozzle discharge. For the measurements on N_2H^+ we have used higher harmonics of klystron radiation in the 60–80 GHz range, that are generated in a Schottky barrier diode. The radiation passes the discharge expansion about 1 to 1.5 cm under the slit and is focused onto an InSb hot electron bolometer. The radiation is frequency modulated and detected at $2f$ by lock in amplification. A fine wire grid is mounted about 2.5 cm under the slit nozzle (see also Fig. 1), which only slightly affects the expansion. This grid is connected to ground. The presence of the grid made the discharge much more stable. Since the discharge produces much electronic noise, the best way to overcome interferences with laboratory equipment is to let vacuum machinery and HV supply share the same ground. This has to be isolated from the laboratory ground circuit.

3. Results and discussion

3.1. NO^+

We have measured the R(8) and R(10) transition in the ground state of NO^+ at 2378.089 and 2385.2328 cm^{-1}, respectively. Using the constants derived by Ho et al. [16] these observed values coincide within the experimental uncertainty with the calculated values. In Fig. 2 the R(10) transition is shown, measured with 8 kHz high voltage modulation. Since diode laser spectroscopy is limited by its mode scanning range of approximately 1 to 1.5 cm^{-1} it is usually impossible to measure subsequent rovibrational transitions for molecules with large rotational constants. Furthermore different modes show different intensity characteristics. For these reasons it was not possible to determine a rotational temperature for the ions produced in this way. However, we expect the ions to be rotationally excited due to collisions. The rather large linewidth (200 MHz) is caused by the poor quality of the laser mode in this range, but we expect the lines to be collisionally broadened as well. Linewidths of the order of 30 MHz, as could be achieved for complexes formed in a slit expansion (Ar–CO [22] and $(CO)_2$ [24]), proba-

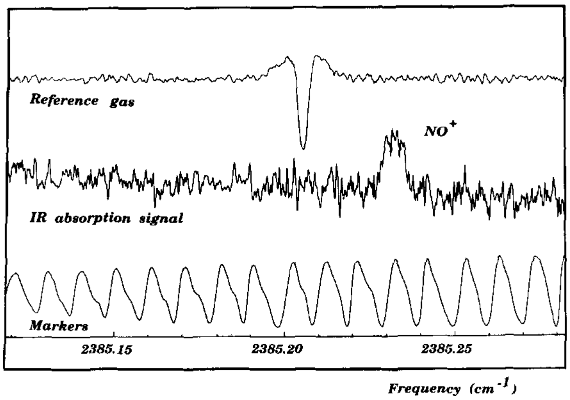

Fig. 2. The P(10) transition for NO$^+$ measured in a crossed jet setup. The upper line shows the reference gas (H_2O), the lower line the marker étalons.

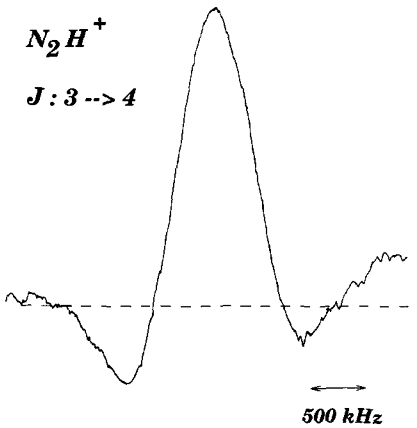

Fig. 3. The $J=3\rightarrow J=4$ transition for N_2H^+ measured in the slit nozzle discharge (RC=10 s).

bly cannot be achieved in this way. On the contrary this method, using two crossed jets, should be the best way to tackle the excited metastable electronic $^3\Sigma$ state as is described in ref. [21].

3.2. N_2H^+

We have studied the $J=3\leftarrow J=2$ and $J=4\leftarrow J=3$ rotational transitions of N_2H^+ at 279511.7 and 372672.5 MHz. A typical result is shown in Fig. 3.

By reducing the frequency modulation it is possible to obtain a minimal linewidth of 750±50 kHz. This is not as small as is found for neutral expansions (typically 200 kHz) (see e.g. ref. [25]). This is probably due to the higher expansion velocity of the ions, caused by the potential difference between slit and fine metal wire grid and the temperature rise, induced by the discharge.

By comparing the linestrengths of several transitions, it is possible to derive a rotational temperature for the N_2H^+. Starting from a Boltzmann distribution the relative line intensities for two J levels (here $J=2$ and 3) is given by

$$T=(E_{J_2}-E_{J_1})/k\ln\left[\frac{2J_2+1}{2J_1+1}\frac{I_{J_2}}{I_{J_1}}\left(\frac{\nu_{J_2}}{\nu_{J_1}}\right)^2\right], \qquad (1)$$

where $E_{J_2}-E_{J_1}$ gives the energy difference between the energy levels, k is the Boltzmann constant, I_J gives the line intensity and ν the frequency for the labeled J level. In Table 1 the linestrengths are shown for different frequency modulations and normalized for power deviations. From the results listed we calculate a rotational temperature of 12 K.

From the first measurements with the high-voltage high-pressure slit nozzle discharge we conclude that it is possible to generate rotationally cold ions. In case of a crossed jet setup both linewidth and rotational temperature are influenced by the collisional process. From the results of the far infrared experiment we expect smaller linewidths and substantially lower temperatures. However, to investigate the metastable $^3\Sigma$ state of NO$^+$, this technique is probably the best method to follow, since no $^3\Pi\rightarrow{}^3\Sigma$ emission was found in an expansion where the NO is seeded in the He directly. The diffusion process seems to be essential [26]. In case of the N_2H^+ formation in a discharge nozzle directly, low rotational temperatures can be achieved. Furthermore, since the expansion has a small Doppler width, narrow linewidths can be obtained. Both characteristics are important for a more accurate analysis of spectra. Since slit nozzle expansions form ideal sources for van der Waals

Table 1
Line intensities for $J=3\leftarrow J=2$ and $J=4\leftarrow J=3$ for different modulations

Transition	FM modulation (MHz)	Linestrengths (au)
$J=2\rightarrow J=3$	0.85	11.8
(279511.7 MHz)	1.10	16.6
$J=3\rightarrow J=4$	0.85	9.75
(372672.5 MHz)	1.10	13.45

complexes [27] combination with a discharge will form an effective way for the investigation of weakly bonded radicals (like Ar–OH or Ar–NH) or ion complexes, which until now have not been investigated successfully with infrared and far infrared techniques. Furthermore it turns out that the discharge can be operated relatively easily and that it is stable over long periods (> 10 h). The discharge sometimes shows dark regions between the electrodes, but this can be improved by using more independent electrodes.

We conclude that the high-voltage high-pressure continuous slit nozzle discharge offers a good alternative to the conventional discharge techniques. It has several advantages that will simplify spectroscopic studies. But the main point of interest is that it probably offers the possibility of investigating a class of molecules that could not be studied until now by direct absorption techniques: the radical and ion complexes.

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