

Millimeter wave spectroscopy in a pulsed supersonic slit nozzle discharge

H. Linnartz^{a,*}, T. Motylewski^a, F. Maiwald^b, D.A. Roth^b, F. Lewen^b, I. Pak^b,
G. Winnewisser^b

^a *Institute for Physical Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland*

^b *I. Physikalisches Institut, Universität zu Köln, Zùlpicherstrasse 77, D-50937 Köln, Germany*

Received 1 June 1998

Abstract

A Doppler-free technique for direct absorption spectroscopy of rotationally cold molecular ions in the millimeter wave range is presented. The method uses a double modulation technique, based on a simultaneous modulation of a frequency doubled microwave sweeper and a pulsed slit nozzle, incorporating a discharge in a high-pressure supersonic expansion. The performance is demonstrated with the observation of the hyperfine structure of the $J = 2 \leftarrow 1$ pure rotational transition of N_2H^+ . Further perspectives of the method are discussed. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The most common technique in the infrared and submillimeter range for direct absorption spectroscopy of molecular ions and radicals has been based on electrical discharges in long and cryogenically cooled cells [1]. Uniform plasmas with high molecular densities have been obtained in hollow cathode geometries [2] and magnetically enhanced negative glow discharges [3]. Velocity modulation has further increased the detection limit [4]. However, the spectroscopy suffers from the disadvantages that are typical for cell environments: high rotational temperatures and Doppler-limited resolution. Therefore much effort has been put in recent years into the development of a technique that combines the advantages of plasma generation and supersonic slit nozzle

expansions [5]. The latter provide a Doppler-free environment and combine high molecular densities and long absorption pathlengths with an effective adiabatic cooling. Several methods have been proposed to obtain a stable plasma over the total length of the slit, varying from ablation and photolysis to discharge and electron impact ionization [6]. Doppler-free spectra of rotationally cold radicals [5], ions [7] and recently, ionic complexes [6,8] have been observed, mainly in the infrared and visible region. However, applications in the millimeter wave range are generally missing. This is astonishing, particularly in view of all the far infrared studies that have been reported in the last ten years using slit nozzle expansions for the study of weakly bound molecular complexes [9]. It appears logical to extend direct absorption millimeter wave experiments to ionic complexes as well, as the intermolecular motions are associated with energies typically of the

* Corresponding author. E-mail: linnartz@ubaclu.unibas.ch

order of $3\text{--}50\text{ cm}^{-1}$. In this Letter an attempt in this direction is reported.

2. Experiment

The N_2H^+ ions were produced in a pulsed slit nozzle incorporating a discharge in a high-pressure expansion. The discharge current is adjusted by the applied voltage and limited by a protective resistor. The source was initially developed for cavity ring-down spectroscopy on long unsaturated carbon chains and has been described in Refs. [10,11]. A cross-section is shown for convenience in Fig. 1. The orifice of the slit comprises an insulator, a metal plate, a second insulator and two sharp plates that form the actual slit ($30\text{ mm} \times 250\text{ }\mu\text{m}$, 60° exit angle). A pulsed negative voltage of $\sim 400\text{ V}$ ($300\text{ }\mu\text{s}$) is applied, to the jaws via a $1\text{ k}\Omega$ ballast resistor. The discharge strikes to the inner metal plate that is grounded. In this way an efficient cooling is obtained, as the localized discharge before the expansion

does not interfere with the subsequent cooling in the expansion. This is an important advantage compared to previously developed systems [12,13] where the plasma is formed in the expansion. The geometry furthermore prohibits HV arcing to the pulsed valve (28 Hz , $350\text{ }\mu\text{s}$), which is mounted on top of the body and regulates the gas flow into the nozzle. Typically flows of 200 ml H_2 , 50 ml N_2 and 500 ml He per minute with a total backing pressure of 3 bar were used. The nozzle is located in a glass cross-piece that is evacuated by a $500\text{ m}^3/\text{h}$ roots blower system to achieve background pressures of $\sim 0.1\text{ mbar}$ during jet operation.

The discharge source was integrated in the Cologne millimeter and submillimeter wave spectrometer [14]. The tunable radiation in the current experiment is generated by a microwave sweeper ($78.33\text{--}118.1\text{ GHz}$) and higher frequencies are obtained by generating higher harmonics in a broadband frequency multiplier with a Schottky barrier diode [15]. The output of the multiplier is guided by a set of lenses through the jet ($\sim 5\text{ mm}$ downstream

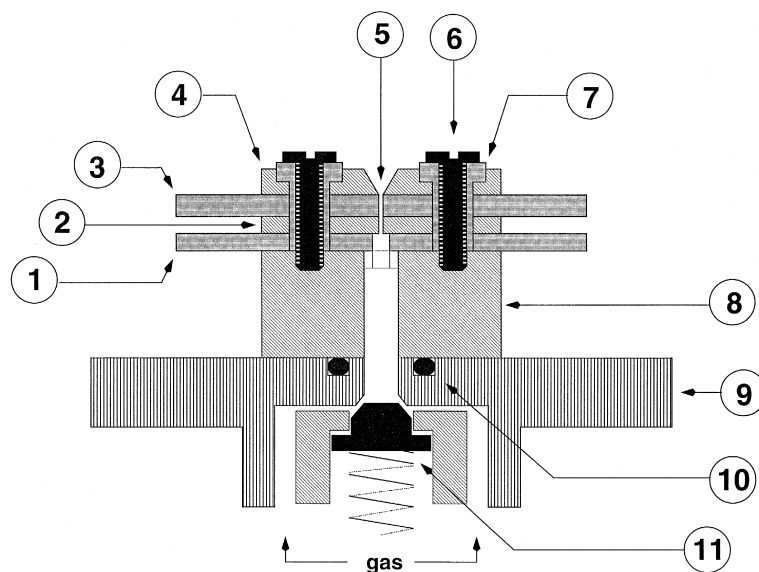


Fig. 1. Cross-section of the high-pressure pulsed supersonic slit nozzle discharge. The orifice consists of a ceramic insulator (1), a metal plate that is grounded (2), a second insulator (3) and two sharp stainless-steel jaws (4) that form the actual slit of $30\text{ mm} \times 250\text{ }\mu\text{m}$ (5). Both insulators and metal parts are mounted to the body of the nozzle by electrically isolated screws (6, 7). A pulsed negative high voltage (-380 V , $150\text{--}300\text{ }\mu\text{s}$) is applied to the jaws via a $1\text{ k}\Omega$ protective resistor in series at the moment that a high-pressure pulse (3 bar) expands through the channel. The discharge strikes to the grounded plate, localizing the reaction zone to a region upstream of the expansion. The floating body of the nozzle (8) is connected to an electro-magnetic driven pulsed valve (9) via an O-ring seal (10). A small plastic poppet (11) controls the gas flow into the nozzle volume.

of the orifice) and is detected by a liquid-helium-cooled InSb detector. The detector signal consists of two types of frequency components; a 20 kHz frequency modulation of the synthesizer and a 28 Hz modulation of the jet. To effectively compensate for the low-duty cycle in the pulsed expansion ($\sim 1\%$), the 20 kHz FM signal is demodulated using lock-in techniques ($t_{RC} = 0.7$ ms) and recorded using a double-gated boxcar integrator. The second gate is used for background subtraction. The principle of this double modulation technique for the detection of weak absorption signals in a pulsed jet has been described in more detail previously in Ref. [16]. A further reduction of the noise level is obtained by inserting a sharp high-pass filter between the detector and the lock-in.

3. Results and discussion

The protonated nitrogen cation N_2H^+ has been taken as a test case. This molecular ion was initially discovered in space [17] and has been studied in detail in laboratory infrared [18,19] and far infrared [20–22] experiments. The hyperfine splitting con-

stants are known from high-resolution work on the $J = 1 \leftarrow 0$ pure rotational transition around 93.174 GHz [23]. More accurate values were obtained in a recent radio-astronomical study [24]. The hyperfine structure of the $J = 2 \leftarrow 1$ transition can be predicted with these constants, but was not observed until now, presumably because a method that combines Doppler-free spectroscopy in a frequency range above 120 GHz was missing.

In Fig. 2 an accumulated spectrum of ten subsequent scans is shown. The bars show the line positions and relative line intensities of the six hyperfine components that are expected from the quadrupole interaction of the outer nitrogen atom, using the value for eqQ as derived in Ref. [24]. The inset shows all 26 components that arise when the inner quadrupole is taken into account as well. These splittings cannot be resolved and cause the overall pattern to be broadened. In Table 1 the line position of the $(F'_1, F_1) = (1, 1)$ is listed as well as the averaged value for the partially resolved $(2, 1)/(3, 2)$ and unresolved $(2, 2)/(1, 0)$ components. The $(1, 2)$ transition is too weak to be observable. The hyperfine structure constants can be derived by fitting these frequencies together with the previous astronomical

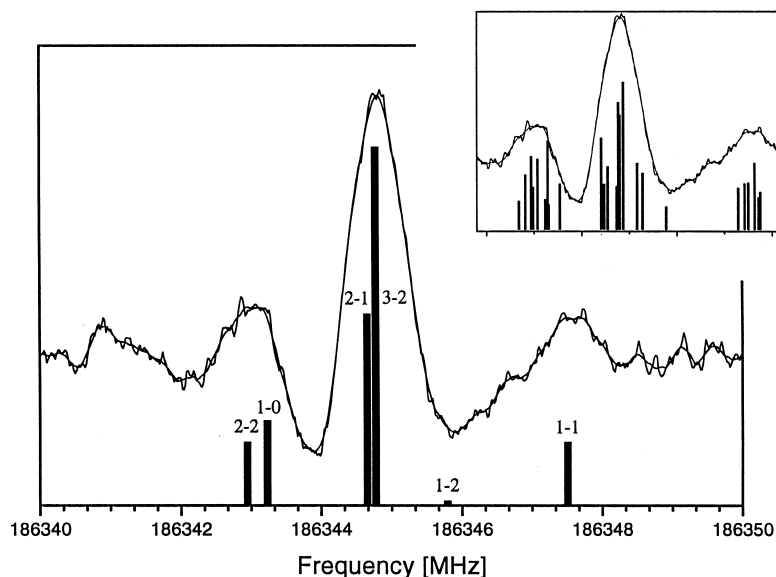


Fig. 2. The partially resolved hyperfine structure of the $J = 2 \leftarrow 1$ pure rotational transition of N_2H^+ , measured in a supersonic slit nozzle plasma. The bars show the expected hyperfine structure components when only the quadrupole of the outer nitrogen is considered. The inset shows the hyperfine structure when the quadrupole interaction of both inner and outer nitrogen is taken into account.

Table 1
Observed hyperfine structure components of the $J = 2 \leftarrow 1$ pure rotational transition of N_2H^+

$F_1' \leftarrow F_1$	ν_{obs}	ν_{calc}
2–2	186343.054(7)	186342.942
1–0		186343.227
2–1		186344.652
	186344.808(5)	
3–2		186344.774
1–1	186347.524(9)	186347.502

The theoretical values are obtained using the constants as listed in the text. All values are in MHz.

data of the $J = 1 \leftarrow 0$ transition with a hyperfine structure Hamiltonian as used in Ref. [24]. Since the hyperfine pattern is only partially resolved in the current experiment, limiting both the accuracy and number of transitions, only a minor gain in accuracy is obtained, yielding $(\text{eqQ})_{\text{outer N}} = -5.6902(21)$ MHz, $(\text{eqQ})_{\text{inner N}} = -1.3583(29)$ MHz, $C_{\text{outer N}} = 0.01175(42)$ MHz and $C_{\text{inner N}} = 0.00868(52)$ MHz. The use of these frequencies in a rotational fit does not improve the values found for B and D in Ref. [21].

From previous experiments around 200 GHz on neutral complexes, linewidths of the order of 300–400 kHz are expected [16]. The (1.0 ± 0.1) MHz linewidth found here is due to unresolved hyperfine structure. The signal to noise ratio of the strongest component amounts to ~ 17 , which explains why the $J = 1 \leftarrow 0$ transition could not be observed with the current apparatus, especially, when the low rotational temperature typical for this type of expansion (~ 20 K [10]) is taken into account.

Due to the limited time in which the Basel and Cologne apparatus could be combined, many possible optimizations were not performed. The low pumping rate of $500 \text{ m}^3/\text{h}$ allowed only moderate backing pressures. The lack of a multipass system limited the total effective absorption pathlength to 3 cm. Whereas high voltages of the order of 3 kV (300–500 mA) are normally used in hollow cathode devices, here < 400 V at 20 mA is applied. This restriction is mainly due to sparks in the vacuum chamber that occur for larger voltages and that cause the detection scheme to go into overload. The nega-

tive high voltage on the jaws is necessary for stable plasma conditions, as has been pointed out in Ref. [5], but for the production of positive ions this may be less favourable. However, even under these conditions signal to noise ratios are obtained that are comparable to conventional techniques, with a resolution that is typically a factor 2 better and with a rotational temperature that is an order of magnitude lower. Taking these factors into account and comparing the result with former data obtained in discharge cells, an absolute density of $\sim 10^{11} \text{ N}_2\text{H}^+/\text{cm}^3$ is estimated in the probe zone. From recent experiments on Ar-HCO^+ and Ar-HN_2^+ [6,8] complexation factors between 5 and 15% have been found, yielding estimated densities for such complexes of the order of 0.5×10^{10} to $1.5 \times 10^{10} \text{ cm}^{-3}$.

Whereas it is clear that this technique offers a good alternative to conventional millimeter wave methods for the study of molecular ions, it is expected that the current method should be also sensitive enough to allow direct absorption spectroscopy of ionic complexes. Especially, when the points mentioned above are improved in future experiments. The extension to the submillimeter wave range will give direct access to the spectroscopy of intermolecular motions, as has been demonstrated in numerous studies on weakly bound neutral complexes. This will be of interest, particularly in view of the role that ionic complexes are thought to play in chemical processes as reactive intermediates; a detailed characterization of the intermolecular energy potential surfaces in this case will give direct information on chemical reactions at the fundamental level of molecular motions.

Acknowledgements

The authors thank E. Klisch and H. Müller for help in recalculating the hyperfine structure constants. This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) via grants SFB301 and WI391/7-1, the Ministerium für Forschung und Technologie des Landes Nordrhein–Westfalen, and the Swiss National Science Foundation (project number 20-29104.96).

References

- [1] E. Hirota, Chem. Rev. 92 (1992) 141.
- [2] F.C. van den Heuvel, A. Dymanus, Chem. Phys. Lett. 92 (1982) 219.
- [3] F.C. De Lucia, E. Herbst, G. Plummer, G. Blake, J. Chem. Phys. 78 (1983) 2312.
- [4] C.S. Gudeman, M.H. Begemann, J. Pfaff, R.J. Saykally, Phys. Rev. Lett. 50 (1983) 727.
- [5] S. Davis, D.T. Anderson, G. Duxbury, D.J. Nesbitt, J. Chem. Phys. 107 (1997) 5661.
- [6] T. Speck, H. Linnartz, J.P. Maier, J. Chem. Phys. 107 (1997) 8706, and references therein.
- [7] T. Ruchti, T. Speck, J.P. Connelly, E.J. Bieske, H. Linnartz, J.P. Maier, J. Chem. Phys. 105 (1996) 2591.
- [8] H. Linnartz, T. Speck, J.P. Maier, Chem. Phys. Lett. 288 (1998) 504.
- [9] D.J. Nesbitt, Annu. Rev. Phys. Chem. 45 (1994) 367.
- [10] D.A. Kirkwood, H. Linnartz, M. Grutter, O. Dopfer, T. Motylewski, M. Pachkov, M. Tulej, M. Wyss, J.P. Maier, Faraday Discuss. 109 (1998) in press.
- [11] H. Linnartz, T. Motylewski, J.P. Maier, J. Chem. Phys. (1998) in press.
- [12] G. Hilpert, H. Linnartz, M. Havenith, J.J. ter Meulen, W.L. Meerts, Chem. Phys. Lett. 219 (1994) 384.
- [13] Y. Xu, M. Fukushima, T. Amano, A.R.W. McKellar, Chem. Phys. Lett. 242 (1995) 126.
- [14] M. Hepp, W. Jaeger, I. Pak, G. Winnewisser, J. Mol. Spectrosc. 176 (1996) 58.
- [15] F. Maiwald, F. Lewen, B. Vowinkel, W. Jabs, D.G. Paveljev, M. Winnewisser, G. Winnewisser, IEEE (in preparation).
- [16] I. Pak, M. Hepp, R. Philipp, R. Schieder, G. Winnewisser, Z. Naturforsch. 49a (1994) 913.
- [17] B.E. Turner, Astrophys. J. 193 (1974) L83.
- [18] C.S. Gudeman, M.H. Begemann, J. Pfaff, R.J. Saykally, J. Chem. Phys. 78 (1983) 5837.
- [19] S.C. Foster, A.R.W. McKellar, J. Chem. Phys. 81 (1984) 3424.
- [20] K.V.L.N. Sastry, P. Helminger, E. Herbst, F.C. de Lucia, Chem. Phys. Lett. 84 (1981) 286.
- [21] P. Verhoeve, E. Zwart, M. Versluis, M. Drabbels, J.J. ter Meulen, W.L. Meerts, A. Dymanus, D.B. McClay, Rev. Sci. Instrum. 61 (1990) 1612.
- [22] M. Havenith, E. Zwart, W.L. Meerts, J.J. ter Meulen, J. Chem. Phys. 93 (1990) 8446.
- [23] G. Cazzoli, G. Corbelli, C. Degli Esposti, P.G. Favero, Chem. Phys. Lett. 118 (1985) 164.
- [24] P. Caselli, P.C. Myers, P. Thaddeus, Astrophys. J. 455 (1995) L77.