

# High resolution infrared direct absorption spectroscopy of ionic complexes

Harold Linnartz,<sup>a)</sup> Dorinel Verdes, and Thomas Speck<sup>b)</sup>  
*Institute for Physical Chemistry, Klingelbergstrasse 80, CH-4056 Basel, Switzerland*

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A sensitive and generally applicable technique for high resolution infrared spectroscopy of weakly bound ionic complexes is presented. The method is based on the direct absorption of tunable diode laser radiation in an expansion cooled planar plasma. The plasma is generated by electron impact ionization of gas that is expanded supersonically through a long and narrow slit. This technique allows a fast and effective production modulation. Online monitoring by a quadrupole mass spectrometer yields direct information on the plasma characteristics. Rotational temperatures as low as 15 K and densities of the order of  $10^9$ – $10^{10}$  complexes/cm<sup>3</sup> are routinely obtained. The technique is discussed on the example of  $N_4^+$  and demonstrated with results on the proton bound complexes  $N_2-H^+-N_2$ ,  $Ar-HN_2^+$ , and  $Ar-HCO^+$ . © 2000 American Institute of Physics.  
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## I. INTRODUCTION

Within the last two decades new experimental and theoretical techniques have been developed which permit the investigation of weak intermolecular forces at an unprecedented level of detail. A good knowledge of these forces—typically van der Waals interactions, hydrogen bonds, and long range electrostatic interactions—is essential for the understanding of the chemical and physical properties of matter. However, whereas weakly bound *neutral* complexes have been studied extensively in the past,<sup>1</sup> high resolution direct absorption spectra of polyatomic *ionic* complexes are only available for a few systems and mainly limited to the submillimeter<sup>2,3</sup> and microwave (MW) range.<sup>4,5</sup> The importance of this type of complexes in chemistry is indisputable;<sup>6,7</sup> ionic complexes are known to play a key role as intermediates in many processes and an accurate spectroscopic characterization would give information on chemical reactions at the fundamental level of molecular motion. Due to their charged nature ionic clusters tend to have binding energies that are in between pure van der Waals and stable covalent bounds, typically 1000–5000 cm<sup>-1</sup> and as a consequence tunnel motions are less pronounced than in their neutral counterparts. This makes spectroscopic assignments less complicated but systematic studies have been historically rare as a technique that produces ionic complexes in large abundances has been lacking.

Most of the available spectroscopic information on ionic complexes to date is based on lower resolution spectra obtained from predissociation studies;<sup>8–10</sup> an ionic complex is mass selected, resonantly excited and the spectrum is observed by monitoring fragment ions mass spectrometrically. Although sensitive and consequently very successful, the technique has the disadvantage that only transitions above

the dissociation limit can be observed. This makes it useless for microwave and submillimeter studies, i.e., those frequency domains that directly probe the inter- and intramolecular dynamics of the complex. In the infrared (IR) region the technique is experimentally limited both in resolution ( $>0.02$  cm<sup>-1</sup>) and frequency range ( $>2500$  cm<sup>-1</sup>), i.e., several fundamentals including the CO and NO stretch cannot be observed directly and the only way to get spectroscopic access is by observing overtone or combination bands. Consequently, many efforts have been put in the development of a sensitive and a generally applicable technique that overcomes these problems. The solution has been sought mainly in direct absorption experiments in expansion cooled plasmas, initially in circular<sup>11</sup> later in slit nozzle geometries.<sup>12</sup> The latter combine high molecular densities and a low final temperature with a relatively long absorption path length. The combination with a reactive plasma meets the principal conditions required for the formation and detection of weakly bound charged complexes. Different techniques, both continuous and pulsed, have been proposed to obtain stable plasmas over the total length of the slit, varying from ablation<sup>13</sup> and photolysis<sup>14</sup> to discharge<sup>15,16</sup> and electron impact.<sup>17</sup> Molecular ions and radicals have been observed in high resolution employing these techniques (see, e.g., Refs. 18–20) but the routine investigation of weakly bound ionic complexes has become possible only recently. As the technique is based on direct absorption it will be useful in other frequency ranges as well. This may be of particular interest to the submillimeter and far IR as these frequency regimes directly probe intermolecular interactions. Detailed spectroscopic information also offers a sensitive check of state-of-the-art calculations on charge induced phenomena which may give new insights in a class of molecules that is expected to be of fundamental importance in all day chemical processes.

## II. EXPERIMENT

The experimental setup is shown schematically in Fig. 1. Tunable radiation (1550–2650 cm<sup>-1</sup>) is generated in a com-

<sup>a)</sup>Electronic mail: linnartz@ubaclu.unibas.ch

<sup>b)</sup>Present address: Physique des Atomes, Lasers, Molécules et Surfaces, U.M.R. du C.N.R.S. No. 6627, Université de Rennes I, 35042, Rennes, France.

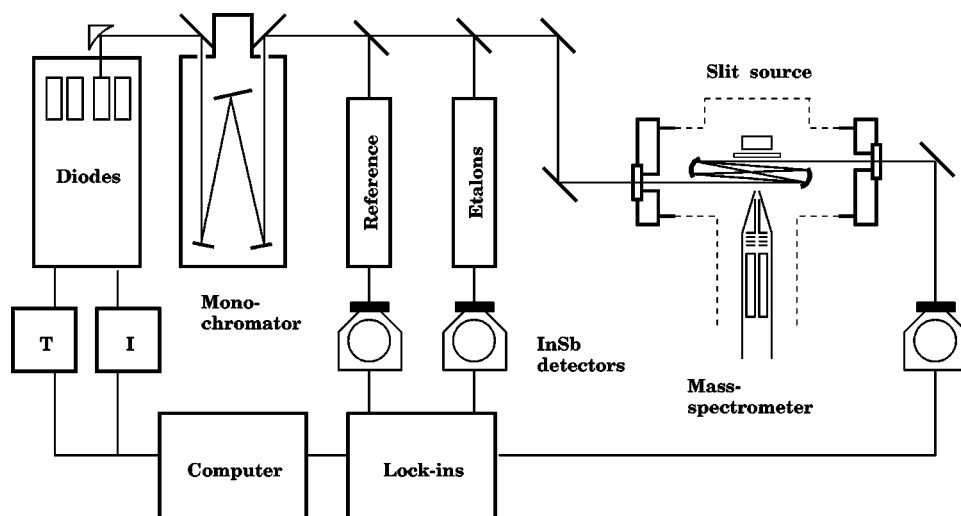


FIG. 1. Schematic diagram of the experimental setup.

mercially available IR spectrometer (Spectra Physics, model 5250) by varying the current and temperature of selected lead-salt diodes. Single mode operation is guaranteed by a monochromator. Part of the infrared beam is guided via beam splitters through a reference gas cell and an étalon that are used for absolute and relative frequency calibration, respectively. In this way an absolute accuracy better than  $0.001 \text{ cm}^{-1}$  is routinely obtained. The main part of the laser beam is guided via a system of mirrors and lenses into a vacuum system and multipasses an approximately 3 cm long planar jet. The vacuum system is evacuated by a roots blower system ( $2150 \text{ m}^3/\text{h}$ ) backed by a  $120 \text{ m}^3/\text{h}$  rotary pump providing a pressure better than 0.2 mbar during jet operation. The total effective absorption path length is increased to roughly 0.5 m by a Perry optical arrangement.<sup>21</sup>

The supersonic plasma is generated by electron impact ionization of gas that is expanded under pressure (typically 1 bar) through a long and narrow slit ( $32 \text{ mm} \times 50 \mu\text{m}$ ) into a vacuum chamber. A detailed view of the system is shown in Fig. 2. The electrons are emitted by a heated tungsten wire (diameter 0.2 mm) that is mounted parallel to and slightly below the slit. It carries a current of typically 4 A which is sufficient to heat the filament to  $\approx 1500 \text{ K}$ . Hypodermic tubing is used to keep the filament straight as it warms up and to guarantee a good electrical contact. The filament is positioned in a slotted tube made of molybdenum that is put on the same negative potential as the filament in order to direct the electrons towards the jet. A slotted stainless steel shield, kept at earth potential is mounted just above the tube in order to accelerate the electrons towards the jet and to shield the expansion zone from residual electrical fields. Ceramic (Macor™) parts are used to effectively isolate the different parts. The filament unit is mounted on a copper block that is water cooled. This copper block is attached to a translation stage that varies the distance from filament to nozzle orifice. The whole assembly is mounted on a second translation stage that varies the distance from orifice to probe laser beam.

The plasma is sampled through a small skimmer ( $200 \mu\text{m}$  orifice) by a quadrupole mass spectrometer that is mounted downstream in a separate differentially pumped vacuum system (pressure  $< 5 \times 10^{-5}$  mbar during jet opera-

tion) in order to optimize the plasma conditions for a specific mass. The assembly has been constructed aerodynamically to avoid disruption of the flow characteristics of the jet. In Fig. 3 a typical mass spectrum for an Ar/CO/H<sub>2</sub> mixture is shown demonstrating the complex distribution of the generated species. Besides Ar-HCO<sup>+</sup> more exotic complexes as  $[(\text{CO})_2\text{H}_3]^+$  are observed. The average densities in the laser probe zone are estimated from the complexation factor (about 7% for Ar-HCO<sup>+</sup> and 12% for Ar-HN<sub>2</sub><sup>+</sup>) by comparing the signal of the bare chromophore to the complexed one. This yields densities of approximately  $5 - 10 \times 10^9$  ionic complexes/cm<sup>3</sup>. Without H<sub>2</sub> in the expansion strong Ar-CO<sup>+</sup> and (CO)<sub>2</sub><sup>+</sup> mass signals are observed. The number of neutral radicals and radical complexes will be significant as well but these are not monitored by the mass spectrometer. It is not possible with the present setup to discriminate directly between neutral and charged species, as it would be when applying velocity modulation,<sup>22,23</sup> but linear scaling of the absorption and mass signal generally allows an unambiguous identification. Instead, an effective production modulation is used by applying a sinusoidal voltage between 0 and -150 V to the filament and the molybdenum tube which switches the plasma on and off very rapidly, up to an frequency of 15 kHz. This modulation technique has the advantage that it is insensitive to baseline fluctuations (étalons) caused by reflections between optical components and the

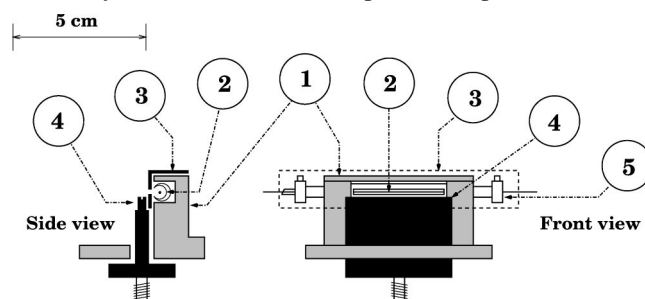


FIG. 2. Schematic side and front view (scaled) of the electron impact slit jet source. The whole system is mounted on a copper block that is water cooled (1). A heated tungsten wire that is mounted in a slotted molybdenum tube (2) emits via a slotted Wehnelt shield (3) electrons towards a ( $32 \text{ mm} \times 50 \mu\text{m}$ ) slit (4). The filament is mounted using ceramic isolators and hypodermic tubing (5).

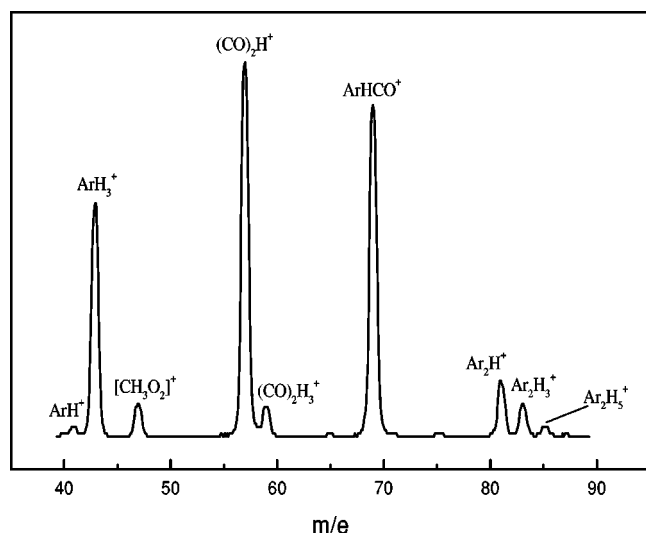


FIG. 3. The mass spectrum showing the ionic species produced in a slit expansion of Ar, H<sub>2</sub>, and CO with electron impact ionization. [Reprinted from H. Linnartz *et al.*, Chem. Phys. Lett. **288**, 504 (1998) with permission from Elsevier Science.]

laser diode, as is often the case for frequency modulation. Noise caused by the background emission of the plasma is low and is further reduced by an infrared bandpass filter in front of the detector. Consequently, there is no need for complicated double modulation schemes as proposed in Ref. 24 to decrease source noise. The detector signal is preamplified and phase sensitively recorded using lock-in techniques.

The plasma current ( $\approx 25$  mA) is measured via a small resistor (8  $\Omega$ ) which offers the possibility to correct for gradual changes in the plasma characteristics that may occur due to filament degeneracy. Particularly hydrogen containing and corrosive plasmas tend to initiate reactions on the *W*-filament's surface, effectively decreasing the diameter of the wire until it breaks. This also limits the effective measuring time for this kind of plasmas to typically 1 to 1.5 h. A self-regulating resistor is used to limit the current during the gradual decay of the filament.

### III. RESULTS

In the next paragraph the jet characteristics are discussed on the example of N<sub>4</sub><sup>+</sup>. Additional results are presented—in a decreasing order of the binding energy—for the proton bound complexes N<sub>2</sub>-H<sup>+</sup>-N<sub>2</sub>, Ar-HN<sub>2</sub><sup>+</sup> (NH and NN stretch) and Ar-HCO<sup>+</sup> (CO stretch).

#### A. N<sub>4</sub><sup>+</sup>

The first infrared data on N<sub>4</sub><sup>+</sup> were obtained after isolating the ion in a 5 K Ne matrix.<sup>25</sup> A broad band around 2237.6 cm<sup>-1</sup> was assigned to the IR active antisymmetric (a.s.) stretching vibration ( $\nu_3$ ) and by analyzing the spectra of <sup>15</sup>N substituted species it was concluded that N<sub>4</sub><sup>+</sup> must have a linear and centrosymmetric ground state structure. This was confirmed by accurate gas phase measurements using the method described here.<sup>26</sup> As N<sub>4</sub><sup>+</sup> is rather strongly bound ( $\approx 1$  eV)<sup>27</sup> the production in a pure N<sub>2</sub> plasma is rather straight forward. The band origin is found at 2234.5084(4) cm<sup>-1</sup>, shifted  $\sim 3$  cm<sup>-1</sup> to lower energy of the

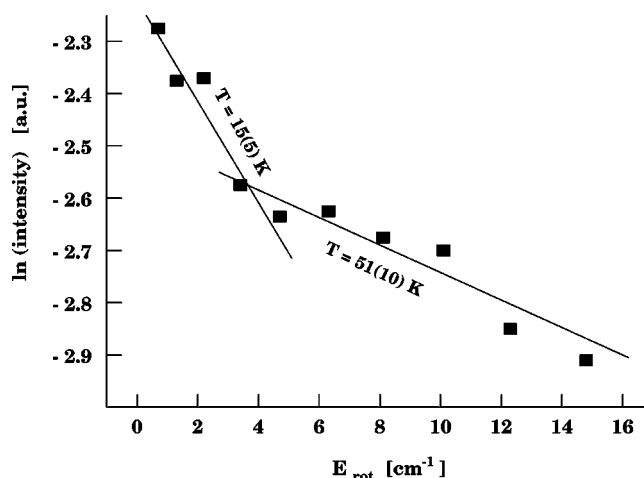


FIG. 4. Boltzmann plot for the power and spin weight corrected  $P(2)$  to  $P(11)$  transitions of N<sub>4</sub><sup>+</sup>, indicating a  $T_{\text{rot}}$  of 15 K for the primary and about 50 K for the secondary temperature regime of the expansion.

matrix value. In total more than 60 rotational lines of the  $\nu_3$  antisymmetric stretch were found. Best signal-to-noise (S/N) ratios are over 100 for typical modulation frequencies of 10 kHz and a filament-orifice distance that was kept as small as possible. The full width at half maximum (FWHM) is  $\sim 120$  MHz, which is slightly larger than the typical laser bandwidth ( $\sim 50$  MHz) and which is due to residual Doppler broadening in the Perry multipass arrangement. The spectrum shows the ordered structure of a  $\Sigma-\Sigma$  transition of a linear molecule, with  $P$  and  $R$  branches and a band gap of approximately  $4B$ . For transitions involving low  $J$ -levels rotational temperatures as low as 15 K are achieved (Fig. 4). Higher  $J$  levels cool less effectively but with  $\approx 50$  K the secondary temperature regime of the expansion is still low. *Ab initio* and matrix studies predict that N<sub>4</sub><sup>+</sup> has a  $2^2\Sigma_u^+$  ground state and consequently for a linear and centrosymmetric structure the rotational levels are expected to exhibit a five to four spin weight alternation for odd and even rotational levels, respectively. This alternation has been found indeed after appropriate power normalization and Boltzmann correction in a production stabilized experiment.<sup>28</sup> The latter has become possible by controlling the absolute N<sub>4</sub><sup>+</sup> production via the modulated mass signal. The rotational constants describing ground and  $\nu_3$  excited state are obtained by fitting the observed transitions to

$$\nu_{\text{obs}} = \nu_0 + (B' + B'')m + (B' - B'' - D' + D'')m^2 - 2(D' + D'')m^3 - (D' - D'')m^4, \quad (1)$$

where  $m = -J$  for  $P$  and  $m = J + 1$  for  $R$  branch transitions. The resulting parameter set is listed in Table I. These values are in excellent agreement with the outcome of recent variational calculations of the rovibrational levels.<sup>29</sup> Predictions given there for combination levels involving symmetric and antisymmetric stretching modes may guide future experimental checks of the bending part of the used potential.

The mass spectra not only allow an online control of the production conditions but also give information on the plasma dynamics. As the N<sub>2n</sub><sup>+</sup> mass signals are considerably stronger than the N<sub>2n+1</sub><sup>+</sup> signals, N<sub>4</sub><sup>+</sup> is formed mainly in

TABLE I. Rotational parameter set of ionic complexes measured in direct absorption using a tunable diode laser spectrometer and electron impact ionization in a supersonic slit jet expansion.

	$N_4^+$ a.s. NN	$N_2-H^+-N_2$ a.s. NN	$N_2-D^+-N_2$ a.s. NN	$Ar-HN_2^+$		$Ar-HCO^+$ CO
				NN	NH	
$\nu_0$	2234.508 7(3)	2352.236 4(6)	2357.383 2(10)	2041.180 2(3)	2505.500 0(2)	2135.707 3(4)
$B''$	0.112 07(1)	0.081 809(14)	0.082 110(35)	0.080 861(10)	0.080 872(5)	0.066 431 978(5) <sup>a</sup>
$D''(10^{-8})$	7.2(8)	...	...	5.5(4)	5.5(2)	6.534(5) <sup>a</sup>
$B'$	0.111 78(1)	0.081 444(13)	0.081 596(35)	0.0819 86(10)	0.0817 34(5)	0.066 783 5(18)
$D'(10^{-8})$	7.1(7)	...	...	5.9(4)	4.9(2)	6.534(5) <sup>a</sup>

<sup>a</sup>Value taken from Ref. 5.

ion-molecule recombinations of  $N_2$  and  $N_2^+$ . Consequently, the ion might be used as an infrared probe for its nonpolar precursors, e.g., in planetary atmospheres. The same is true for  $N_2-H^+-N_2$ .

### B. $N_2-H^+-N_2$

In the range around  $2350\text{ cm}^{-1}$  the rotationally resolved band system of the antisymmetric NN stretching vibration ( $\nu_3$ ) of the linear and centrosymmetric  $N_2-H^+-N_2$  has been found.<sup>30</sup> These data represent the first high resolution gas phase data of this cluster ion, as microwave spectra cannot be obtained and IR predissociation results are lacking due to the high binding energy of the complex ( $\approx 0.6\text{ eV}$ ). The complex is rather easily generated in an Ar(90),  $N_2(5)$ , and  $H_2(5)$  mixing ratio but good S/N ratios are prohibited by strong atmospheric  $CO_2$  absorptions, even when the path of the IR beam is purged by nitrogen gas.  $N_2-H^+-N_2$  can be considered as a prototype of cluster ions of the form mol- $H^+$ -mol and in view of the role of molecular nitrogen in planetary atmospheres it may be involved in atmospheric reactions. It was found previously in a mass spectrometric investigation of the equilibrium reaction  $N_2H^+ + N_2 \rightleftharpoons (N_2)_2H^+$ .<sup>31</sup> Early *ab initio* calculations<sup>32</sup> predicted a linear equilibrium structure but only recently it was proven that this is actually the case.<sup>30</sup> This was concluded both from theory and from the small vibrational shift ( $5\text{ cm}^{-1}$ ) observed for the deuterium substituted derivative,  $N_2-D^+-N_2$ . In total 39 and 32 vibration-rotation lines were observed for  $N_2-H^+-N_2$  and  $N_2-D^+-N_2$ , respectively. The ground and excited state constants were evaluated using Eq. (1). Inclusion of the centrifugal distortion constants did not appreciably improve the fit and was left out. The resulting parameter set is listed in Table I. A detailed description of the structural conclusions is available from Ref. 30.

### C. $Ar-HN_2^+$

The linear proton bound  $Ar-HN_2^+$  belongs to the better studied ionic complexes. Pure rotational spectra were reported in an unpublished microwave study<sup>33</sup> and three rotationally resolved vibration bands starting from the ground state were obtained by IR predissociation experiments.<sup>34,35</sup> The assignment of the latter to combination bands involving the shifted  $\nu_1$  (NH) and intermolecular stretch ( $\nu_s$ ) was based on assuming an approximately linear relationship between the complexation induced redshift of the fundamental and the proton affinity of the rare gas partners. The band

with lowest wavenumber at  $2505\text{ cm}^{-1}$  was assigned to the  $\nu_1 + \nu_s$ , which implies a frequency for the NH fundamental around  $2285\text{ cm}^{-1}$ , outside the range of standard IR predissociation experiments but within that of the present one. However, even after scanning the  $2200\text{--}2400\text{ cm}^{-1}$  range systematically the  $\nu_1$  fundamental was not found.<sup>36</sup> Instead, following theoretical predictions<sup>37</sup> a very strong band system was found around  $2040\text{ cm}^{-1}$ , representing vibrational excitation of the NN stretching vibration of the chromophore. In Fig. 5 the band origin region of this system is shown, recorded in a mixture identical to that used for  $N_2-H^+-N_2$ . The band was found after state-of-the-art quantum chemical calculations predicted an exceptionally strong anharmonic interaction between the excited NH and NN vibration resulting in an unusually large contribution to the redshift and strong increase in intensity of the band around  $2040\text{ cm}^{-1}$ . The same calculations interpret the band at  $2505\text{ cm}^{-1}$  to originate from the shifted  $\nu_1$  fundamental. As low  $J$  levels do not exceed the energy necessary to dissociate the complex ( $D_0 = 2781.5\text{ cm}^{-1}$ )<sup>34</sup> and consequently are missing in the predissociation experiment, these have been measured with the present technique as well. In total more than 80 transitions for each band have been found.<sup>37,38</sup> The rotational constants for ground state and NN and NH vibrationally excited  $Ar-HN_2^+$ , calculated from Eq. (1) are summarized in Table I. As both vibrational bands start from the ground state the values for  $B''$  and  $D''$  should overlap within their  $1\sigma$  uncertainties, which is clearly the case. More details on the involved anharmonicity will be available from Ref. 37.

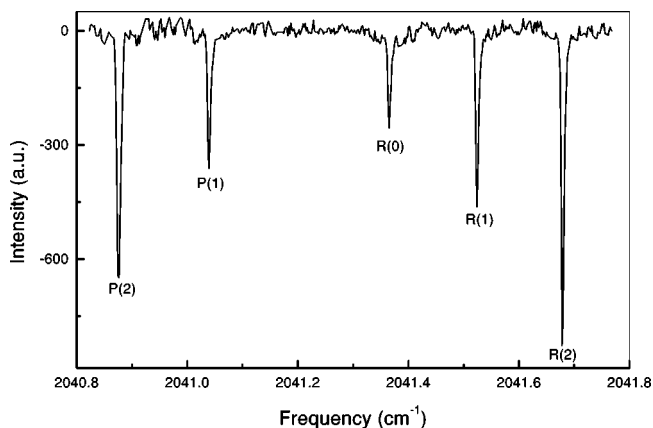


FIG. 5. The band origin region of the excited NN stretching vibration of  $Ar-HN_2^+$ , recorded in direct absorption by tunable diode laser spectroscopy in a supersonic planar plasma.

## D. Ar–HCO<sup>+</sup>

The spectroscopic properties of the Ar–HCO<sup>+</sup> have been studied by exciting the CO stretch of the HCO<sup>+</sup> chromophore around 2135 cm<sup>-1</sup>.<sup>39</sup> In total more than 60 rotational transitions have been found. As for Ar–HN<sub>2</sub><sup>+</sup> the spectrum has a structure consistent with a linear proton-bound complex. The ground state rotational progression is calculated from combination differences and fits within the experimental uncertainty with the values based on the available microwave constants.<sup>5</sup> The complete data set is fit, using Eq. (1) and fixing the ground state constants to the MW results. This gives the constants listed in Table I. Under the assumption that the chromophore unit is undistorted upon excitation an Ar–H separation of 2.135 Å for the ground and 2.125 Å for the excited state is calculated. The latter is about 0.04 Å longer than the proton-argon separation found on excitation of the  $\nu_1$  (CH) stretch in a previous predissociation experiment.<sup>40</sup> This is expected as the CH stretch is directly involved in the intermolecular bond. For the same reason the origin band position for the excited CO stretching vibration shifts 48.24 cm<sup>-1</sup> whereas for the excited CH stretching vibration a larger shift of 274 cm<sup>-1</sup> is found.<sup>40</sup> These values agree very well with the outcome of a theoretical study<sup>41</sup> that also predicts harmonic frequencies for the combination tones of the CO stretching vibration with the intermolecular stretching and bending modes around 2250 cm<sup>-1</sup>. Experiments to detect these weak modes are in progress.

## ACKNOWLEDGMENT

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