Mid-infrared continuous wave cavity ring down spectroscopy of molecular ions using an optical parametric oscillator

H. Verbraak [a], A.K.Y. Ngai [b], S.T. Persijn [b], F.J.M. Harren [b], H. Linnartz [a,*]

[a] *Sackler Laboratory for Astrophysics, Leiden Observatory, Leiden University, Postbus 9513, NL-2300 RA Leiden, The Netherlands*
[b] *Life Science Trace Gas Facility, Molecular and Laser Physics, Institute for Molecules and Materials, Radboud University, P.O. Box 9010, NL-6500 GL Nijmegen, The Netherlands*

Abstract

A sensitive infrared detection scheme is presented in which continuous wave cavity ring down spectroscopy is used to record rovibrational spectra of molecular ions in direct absorption through supersonically expanding planar plasma. A cw optical parametric oscillator is used as a light source and combines a broad spectral coverage (2100–3600 cm^{-1}) and narrow bandwidth (7 kHz) with a high output power (~ 1 W) and excellent TEM_{00} mode characteristics. The performance of the technique is demonstrated by recording a rotationally cold spectrum of formyl cation, HCO^+, in the CH stretching region. For optimal conditions, absolute ion densities in the plasma expansion amount to 2×10^{10} HCO^+-ions/cm^3 in the detection zone.
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1. Introduction

Molecular ions are reactive species that govern the chemical properties of plasma, as found in interstellar clouds, combustion processes and the upper layers of our atmosphere. Spectral fingerprints are necessary to determine the structural and dynamical parameters of these ions as well as to identify molecular transients in highly reactive environments. Their instability, however, also complicates systematic laboratory studies, mainly because of difficulties that are related to the production of ions in high abundances. Consequently sensitive detection techniques are needed in combination with effective production techniques, typically long and cryogenically cooled cell discharges [1–3] and supersonic plasma expansions [4–8]. Moreover a narrow linewidth and broad tunability of the light source are needed in order to resolve the rotational structure and to cover large frequency domains. Particularly in the mid-infrared – the molecular fingerprint region –

this combination has hampered systematic spectroscopic studies of molecular ions. Nevertheless, in the last two decades a number of very successful techniques have been developed. Cluster ions have been studied intensely using dissociation techniques [9,10]. Other detection schemes use the short lifetime, the net charge or open shell character of a molecular ion in sophisticated phase sensitive detection schemes, following for example production [7], velocity [11] or Zeeman modulation [12]. Also straightforward frequency or special double modulation schemes have been reported [13,14]. More recently cavity enhanced absorption techniques have been proposed as a powerful alternative based upon direct absorption principles [15]. However, whereas searches for high resolution spectra of transient species by cavity ring down (CRD) spectroscopy are becoming routine in the UV/VIS [16], applications in the mid-infrared are limited and essentially lacking for molecular ions. (We are only aware of cw-CRD measurements of H_3^+ and D_2H^+ in the near infrared using discharge cells [17,18].)

Until recently, this has been due to a general lack of affordable mirrors with sufficiently high reflectivity as well as missing fast infrared detectors. In addition, an extension

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to cw-CRD techniques has remained problematic because the standard infrared lasers either have a good mode profile but suffer from poor tunability (e.g. CO_2/CO lasers [19] and quantum cascade lasers [20]) or have good spectral coverage but poor mode characteristics (e.g. diode lasers) [21,22]. The cw-OPO system used in this work overcomes this problem and, in addition, has a superb TEM_{00} mode profile which is a prerequisite for routine cw-CRD work. The combination with a planar expansion facility provides a unique tool for sensitive and selective high resolution spectroscopy at rotationally cold temperatures [23]. This letter describes this generally applicable method to record infrared spectra of molecular ions and the performance is discussed on the example of a rotationally resolved infrared CH-stretch (ν_1) spectrum of formyl cation, HCO^+.

2. Experiment

A schematic of the experimental setup is given in Fig. 1. The HCO^+ ions are produced in a supersonic planar plasma expansion that has been described in much detail recently [24]. A gas mixture of Ar, H_2 and CO (90:5:5 mixture) is expanded continuously with 600 mbar backing pressure through a slit (3.2 cm × 50 μm) into a vacuum chamber, that is evacuated by a strong roots blower system with a total pumping capacity of 4800 m^3/h. The gas is subsequently bombarded by electrons that are emitted from a heated tungsten wire (−120 V, 4 A) that is positioned in a slotted molybdynum tube. In front of the tube a slotted metal plate is placed on ground potential. Emitted electrons are accelerated toward the gas mixture, which is ionized through collisions with the electrons. The resulting plasma is sampled by a quadrupole mass spectrometer via a skimmer with an orifice of 200 μm that is mounted about 3 cm downstream. In this way the plasma is optimized for best HCO^+ production. Besides HCO^+ also cluster ions like Ar–HCO^+ and protonated CO clusters $[(CO)_nH]^+$ are readily formed (see Fig. 2 for a mass spectrum optimized for $[(OC)_2H]^+$). The plasma expansion is monitored by the output of a home-made cw-OPO system
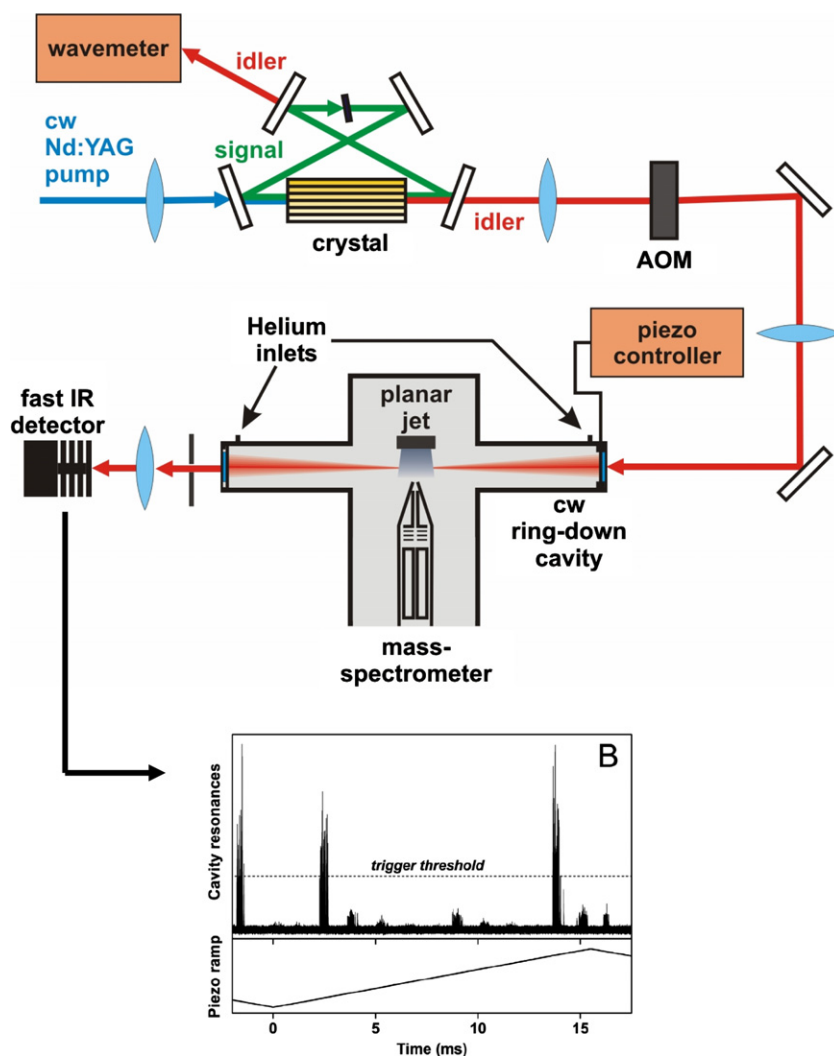

Fig. 1. Schematic overview of the experimental cw-CRD setup (A) in which a planar plasma (Leiden) and cw-OPO laser system (Nijmegen) are combined. Inset (B) shows the transmission characteristics of the cavity when scanning the piezo voltage. The excellent mode characteristics provide an unambiguous setting for the trigger threshold.
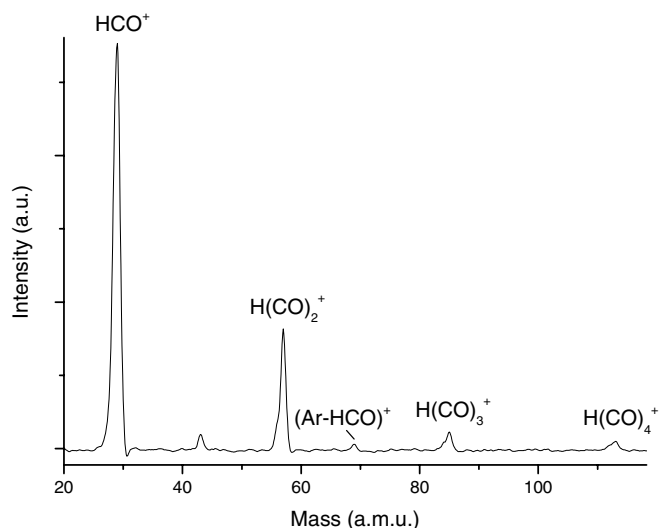
Fig. 2. A quadrupole mass spectrum of expanding Ar/H₂/CO plasma, recorded approximately 3 cm downstream from the nozzle orifice. The plasma has been optimized for HCO⁺ production.

consisting of a standard four-mirror bowtie ring design that has been described in detail in [25].

An MgO-doped periodically poled lithium niobate (PP-MgO-LN) crystal (HC Photonics) is used for the parametric oscillation. The OPO is pumped by a cw-Nd:YAG laser (Lightwave M6000 MOPA) which has an output power of ∼10 W. Although mode hops occur every 12 GHz, the Nd:YAG laser has a continuous tunability of 1.3 cm⁻¹. The frequency can be further tuned by tilting an intracavity etalon in the OPO increasing the tunability to 7 cm⁻¹. Additionally the idler and signal frequency can be changed by altering the temperature or period of the PP-MgO-LN crystal, which allows for scanning the idler and signal frequency between 2100–3600 cm⁻¹ and 5800–7300 cm⁻¹, respectively. The idler frequency is used for the cavity ring down measurements and has an output power of ∼1 W. The resulting bandwidth relevant for the cavity ring down measurements is 7 kHz over 20 μs and 4.5 MHz over 1 s. The mode structure of the system is mainly TEM₀₀, which strongly facilitates the use of cw-CRD as a detection technique, as shown in the inset of Fig. 1.

A standard detection scheme is used to record the ring down events. The method essentially follows the scheme as described in [26,27]. The OPO output is guided through a Germanium acousto-optic modulator (AOM), which deflects 20% of the idler wave under an angle of 15° towards the ring down cavity when switched on. The cavity consists of two mirrors with a reflectivity of 99.98% (Los Gatos Research, see Ref. [25]) between 2960 and 3060 cm⁻¹ that are mounted 60 cm apart. Special helium curtains are used to protect the mirrors from pollution. The cavity is aligned in such a way that the laser beam is parallel to the slit a few mm downstream of the orifice. The cavity length is modulated over one free spectral range at a frequency of 30 Hz by means of a piezo-electric trans-

ducer mounted on one of the mirror holders. In this way the cavity becomes infrared transparent at least once during a piezo scan. When the intensity in the cavity reaches a threshold value the AOM is switched off and a ring down signal occurs that is fitted using a fast exponential fitting algorithm [28]. A spectrum is recorded by measuring the ring down time as function of the frequency. The typical ring down time in the present experiment amounts to about 12 μs and corresponds to approximately 6000 passes or an absorption length of at least 200 m through the expansion. The spectra are calibrated by focusing part of the idler wave on a wavemeter. The combination of a nearly Doppler free environment in a planar expansion, a very narrow bandwidth and an accurate frequency calibration using a wavelength meter (Bristol Instruments 621A), allows an accurate determination of line positions with an absolute accuracy of the order of 5×10^{-4} cm⁻¹.

3. Results and discussion

Fig. 3 shows part of the R-branch of the CH-stretching vibration of HCO⁺ from $J = 0$–5. The transitions observed here were first recorded in 1983 in discharge cells using phase sensitive detection techniques [11,29] and have been used ever since for testing new discharge techniques. Our line positions – $R(0) = 3091.6900$ cm⁻¹, $R(1) = 3094.6176$ cm⁻¹, $R(2) = 3097.5217$ cm⁻¹, $R(3) = 3100.4023$ cm⁻¹, $R(4) = 3103.2582$ cm⁻¹ and $R(5) = 3106.0904$ cm⁻¹ – are accurate up to 0.0005 cm⁻¹ and overlap within the experimental uncertainties with the previously reported values.

The typical full-width-at-half-maximum (FWHM) value amounts to 105 MHz and is determined by residual Doppler broadening in the expansion. This corresponds to a kinetic temperature of 72 K, which is substantially lower than in cell environments. The rotational cooling is determined from a Boltzmann plot to be $T_{\text{rot}} \sim 19$ K. As a direct consequence J-levels with a value higher than $J = 6$ are not sufficiently populated to be detectable.

A specific advantage of cw-CRD is that it is possible to determine absolute densities, once the absorbance (A) is available. In the present experiment this is calculated from the ring down time (τ) [30].

$$A = \frac{n}{c} \times \frac{L}{2.303} \times \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \tag{1}$$

with n the index of refraction (taken as one), c the speed of light, L the distance between the mirrors (0.6 m), 2.303 the conversion factor between natural log and log base 10 and τ_0 the ring down time of the base line (i.e. with plasma on, but without molecular absorption).

It should be noted that the accurate derivation of absolute ion densities from A in plasma sources is important and not straightforward and therefore, the procedure is described in some more detail below. It follows essentially the method described in [31] and applies for a distance of 0.5 mm from the nozzle orifice. For the ν_1 fundamental of HCO⁺ an integrated infrared band intensity (S_ν^0) of
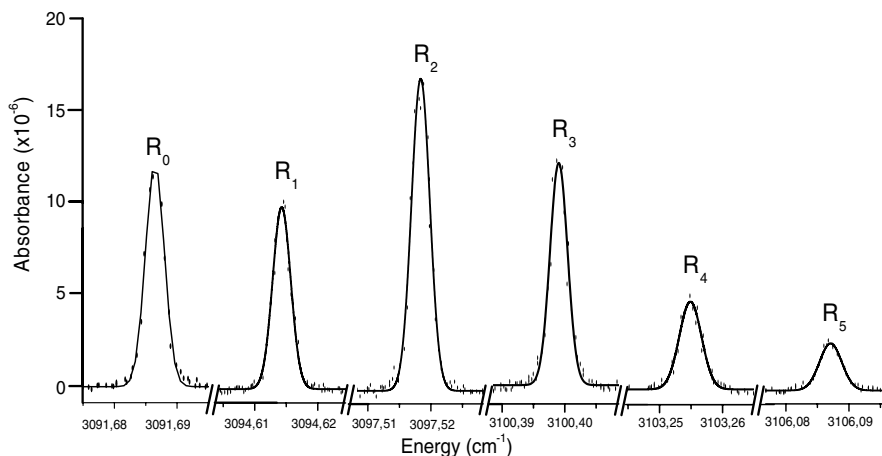
Fig. 3. The $R(0)$–$R(5)$ transitions of HCO^+ observed in direct absorption – directly visualized in absorbance units – through supersonically expanding plasma. A mid-infrared cw-OPO laser system is used as radiation source and cw-CRD is applied as a sensitive detection technique.

(580 ± 90) cm^{-2} atm^{-1} has been reported in [31] using fast ion beams. Eq. (2) shows the formula for determining the HCO^+ ion density

$$[HCO^+] = \left(\frac{\pi}{4 \ln 2}\right)^{1/2} \times A \times \Gamma_D \times \frac{1}{S_{if} \cdot d} \qquad (2)$$

where A is the absorbance as derived from Eq. (1), Γ_D the FWHM (105 MHz = 0.0035 cm^{-1}), S_{if} the integrated line strength for a single rovibrational transition (in cm^{-2} atm^{-1}) and d the actual length of the slit (3.2 cm). The integrated line strength S_{if} and the integrated infrared band intensity S_v^0 are related by

$$S_{if} = S_v^0 \times R_{if} \times F \qquad (3)$$

where R_{if} is the fraction of the total band strength accounted for in a particular rovibrational transition and F the Herman–Wallis vibration–rotation interaction correction which is taken as unity. For linear molecules the expression for R_{if} is

$$R_{if} = |m| e^{-E_{rot}/kT_{rot}} q_{rot}^{-1} \frac{v_{if}}{v_0} (1 - e^{-v_{if}/kT_{vib}}) \qquad (4)$$

with $|m| = J + 1$ for R-branch transitions, E_{rot} the initial rotational energy in the ground state, T_{rot} and T_{vib} the rotational and vibrational temperatures, q_{rot} the rotational partition function $\left(= \sum_J (2J + 1) e^{-BJ(J+1)/kT_{rot}}\right)$, v_{if} the energy of the excited state and v_0 of the band origin. In order to calculate $[HCO^+]$ the integrated line strength S_{if} must be known which is calculated from Eqs. (3) and (4). It is not possible to derive T_{vib} as hot bands are not observed. Typically, in a molecular beam expansion T_{vib} is a few times larger than T_{rot} but in plasma with ongoing electronic excitations and relaxations the value of T_{vib} may become substantially larger [32,33]. Following Eq. (4) a higher T_{vib} will decrease R_{if} (and consequently S_{if}), but only in a very noncritical way. Therefore $T_{vib} = T_{rot}$ has been taken here and the derived values represent lower density limits. The rotational energies are calculated using $B = 1.475699$ cm^{-1} yielding $q_{rot} = 9.29$.

Table 1
Values for R_{if}, S_{if} and resulting ion densities in atm and HCO^+/cm^3 for the planar plasma expansion at about 0.5 mm downstream of the nozzle orifice

J	R_{if}	S_{if}	A (10^{-6})	$[HCO^+]$ $(10^{-10}$ atm$)$	$[HCO^+]$ $(10^{10}$ HCO^+/cm$^3)$
0	0.10764	62.43272	11.4	2.11	2.15
1	0.17233	99.95156	9.5	1.10	1.12
2	0.16563	96.06702	16.9	2.03	2.08
3	0.11327	65.69772	12.1	2.13	2.17
4	0.05813	33.71613	4.8	1.66	1.69
5	0.02292	13.29634	2.3	2.02	2.06

Table 1 lists the resulting $[HCO^+]$ values for the observed J-levels that vary between 1.66 and 2.13 × 10^{-10} atm, with exception of the $J = 1$ value (1.10 × 10^{-10} atm) where we expect that plasma conditions were not fully optimum. The concentration of HCO^+ is converted from units of atm to HCO^+/cm^3 assuming steady gas and stable plasma conditions and taking a translational temperature of 72 K as derived from the Doppler width. This results in an average density of roughly 2×10^{10} HCO^+/cm^3. The absolute value also allows a determination of the other (cluster)ions formed in the plasma through linear scaling of the mass signals (see Fig. 2). For $[(OC)_2H]^+$ a complexation rate of the order of 20–25% is found which corresponds to a density of $\sim 5 \times 10^9$ ions/cm^3. This is substantially higher than the typical complexation rate found for neutral van der Waals complexes ($\sim 5\%$) and reflects the larger binding energies due to charge induced interactions. For the proton bound Ar–HCO^+ – that has not been optimized in the shown test run – still complexation rates of >10% have been found. The latter system has been studied in much detail, but $[(OC)_2H]^+$ spectra are fully lacking and clearly this cannot be due to a production problem. This is unfortunate, as at this stage it is fully unclear whether this molecule has a centro-symmetric 'proton-sandwich' CO–H^+–CO geometry (comparable to N_2–H^+–N_2 [34]) or a more complex struc-

ture like CO–HCO^+. The latter one may be interesting as the intermediate product of two abundant species in ion–molecule reactions in interstellar space.

So far cluster ions have been measured through the plasma source described here by applying a phase sensitive detection scheme following production modulation in combination with tunable diode laser spectroscopy [7,24,34]. The present result shows that a direct absorption technique based upon cw-CRD using an OPO system offers a powerful alternative.

The setup described here also would be suited to quantify reaction dynamical aspects in the expansion. In the last years calculations have been reported that simulate the flow characteristics of expanding planar plasma (see e.g. [35]). For obvious reasons chemical reactivity has not been taken into account in these models. The present setup allows the online probing of densities of different reaction products, by intersecting the plasma at different distances from the nozzle orifice. For a two-dimensional expansion the particle concentration is expected to behave as $1/r$, where r is the distance between laser beam and nozzle orifice and only in a non-reactive environment the product of the concentration and r should give a constant value. It should be noted that the rotational and vibrational temperature also change with distance to the nozzle orifice and that this has to be taken explicitly into account. It has not been possible to study this in detail during the short period, in which the Nijmegen OPO system was available for experiments on the Leiden plasma setup.

Acknowledgements

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