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

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Abstract

A sensitive infrared detection scheme is presented in which continuous wave cavity ring down spectroscopy is used to record rovibrotational 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 TEM00 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 2×10¹¹ HCO⁺-ions/cm³ 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⁺ and D₂H⁺ 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
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. CO₂/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 TEM₀₀ 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 (ν₁) 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, H₂ 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 m³/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 molybdenum 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.
The Nd:YAG laser has a continuous tunability of $1.3 \text{ cm}^{-1}$ (Lightwave M6000 MOPA) which has an output power of $10 \text{ W}$. Although mode hops occur every $12 \text{ GHz}$, the Nd:YAG laser has a continuous tunability of $1.3 \text{ cm}^{-1}$. The frequency can be further tuned by tilting an intracavity etalon in the OPO increasing the tunability to $7 \text{ cm}^{-1}$. 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 $2100–3600 \text{ cm}^{-1}$. The frequency can be further tuned by changing the idler 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 $5 \times 10^{-4} \text{ cm}^{-1}$.

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 – $R(0) = 3091.6900 \text{ cm}^{-1}$, $R(1) = 3094.6176 \text{ cm}^{-1}$, $R(2) = 3097.5217 \text{ cm}^{-1}$, $R(3) = 3100.4023 \text{ cm}^{-1}$, $R(4) = 3103.2582 \text{ cm}^{-1}$ and $R(5) = 3106.0904 \text{ cm}^{-1}$ – are accurate up to $0.0005 \text{ cm}^{-1}$ and overlap within the experimental uncertainties with the previously reported values.

The typical full-width-at-half-maximum (FWHM) value amounts to $105 \text{ MHz}$ and is determined by residual Doppler broadening in the expansion. This corresponds to a kinetic temperature of $72 \text{ K}$, which is substantially lower than in cell environments. The rotational cooling is determined from a Boltzmann plot to be $T_{rot} \sim 19 \text{ K}$. 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 $(\tau)$ [30].

$$A = \frac{n}{c} \times \frac{L}{2.303} \times \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$  \hspace{1cm} (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 $\tau_0$ 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 $v_1$ fundamental of HCO$^+$ an integrated infrared band intensity $(S^0_1)$ of...
(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

$$[\text{HCO}^+] = \left( \frac{\pi}{4 \ln 2} \right)^{1/2} \times A \times \Gamma_D \times \frac{1}{S_0 \cdot d}$$  (2)

where \( A \) is the absorbance as derived from Eq. (1), \( \Gamma_D \) the FWHM (105 MHz = 0.0035 cm⁻¹), \( S_0 \) 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 \( S_0 \) and the integrated infrared band intensity \( S_0^\text{if} \) are related by

$$S_0^\text{if} = S_0 \times R_\text{if} \times F$$  (3)

where \( R_\text{if} \) 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 rotational energy in the ground state, \( T_\text{rot} \), and the rotational and vibrational temperatures, \( q_\text{rot} \) and \( q_\text{vib} \), are related by

$$q_\text{if} = E_{\text{rot}}/kT_{\text{rot}} q_\text{rot}^{-1} q_\text{vib}^{-1}$$  (4)

with \( |m| = J + 1 \) for \( R \)-branch transitions, \( E_{\text{rot}} \) the initial rotational energy in the ground state, \( T_\text{rot} \), and \( T_\text{vib} \) the rotational and vibrational temperatures, \( q_\text{rot} \) the rotational partition function (\( = \sum_{J} (2J + 1) e^{-B(J+1)/kT_{\text{rot}}} \)), \( q_\text{vib} \) the energy of the excited state and \( v_0 \) of the band origin. In order to calculate [HCO⁺] the integrated line strength \( S_0 \) must be known which is calculated from Eqs. (3) and (4). It is not possible to derive \( T_\text{vib} \) as hot bands are not observed. Typically, in a molecular beam expansion \( T_\text{vib} \) is a few times larger than \( T_\text{rot} \) but in plasma with ongoing electronic excitations and relaxations the value of \( T_\text{vib} \) may become substantially larger [32,33]. Following Eq. (4) a higher \( T_\text{vib} \) will decrease \( R_\text{if} \) (and consequently \( S_0 \)) but only in a very non-critical way. Therefore \( T_\text{vib} = T_\text{rot} \) has been taken here and the derived values represent lower density limits. The rotational energies are calculated using \( B = 1.475699 \) cm⁻¹ yielding \( q_\text{rot} = 9.29 \).

Table 1

<table>
<thead>
<tr>
<th>( J )</th>
<th>( R_\text{if} )</th>
<th>( S_0^\text{if} )</th>
<th>( A ) (10⁻⁶)</th>
<th>[HCO⁺] (10⁻¹⁰ atm)</th>
<th>[HCO⁺] (10⁻⁶ HCO⁺/cm³)</th>
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<td>13.29634</td>
<td>2.3</td>
<td>2.02</td>
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</table>

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⁺/cm³ 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 × 10¹⁰ HCO⁺/cm³. 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 ~5 × 10⁹ ions/cm³. This is substantially higher than the typical complexation rate found for neutral van der Waals complexes (~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 N₂–H⁺–N₂ [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 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.

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