High-resolution infrared spectrum of the ν_3 band in Ar–HCO$^+$

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Abstract

Spectroscopic properties of Ar–HCO$^+$ have been studied by exciting the C–O stretch of the HCO$^+$ chromophore. The ionic complex is generated in a slit jet expansion with subsequent electron impact ionization. The spectra are obtained by direct absorption spectroscopy using a tuneable diode laser and production modulation. The ν_3 band of the Ar–HCO$^+$ is rotationally resolved and has a form consistent with a linear proton-bound complex. The band origin is at 2135.7073(4) cm^{-1} which is 48.24 cm^{-1} red-shifted compared to the value in free HCO$^+$. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Ionic complexes play a key role as unstable intermediates in many chemical reactions. However, high-resolution spectroscopic information has been obtained on only a few systems, presumably because a technique that generates cluster ions in high abundance is lacking. ArH$_3^+$ and its isotopomers were observed in a negative glow discharge about 10 years ago [1] and, recently, in supersonic expansions Ar–HCO$^+$ and Ar–HN$_2^+$ were observed using FT microwave and tunable infrared spectroscopy, respectively [2,3].

Most of the available information on ionic complexes to date is based on results of predissociation studies [4–6]. A cluster ion is mass selected and the fragmentation signal is measured after resonant excitation. Although sensitive and consequently successful, the technique has the disadvantage that only transitions above the dissociation limit can be observed. The pulsed laser systems used are limited both in resolution (typically 0.02 cm^{-1} in the in-

frared) and available frequency range (typically > 2500 cm^{-1}). Consequently several fundamentals, including the C–O stretch, cannot be observed directly and the only way to get spectroscopic access is by observing overtone or combination bands. For these reasons many efforts have been put in recent years in the development of a technique that combines high-resolution spectroscopy on ionic complexes with general applicability. The solution has mainly been sought in direct absorption measurements of species generated in stable slit nozzle plasmas. The combination of a slit jet expansion (high molecular densities, low final temperatures and long absorption lengths) and plasmas (radical and ion formation) meets the principal conditions required for the formation and detection of weakly bound charged complexes. Several methods have been proposed based on photolysis [7], ablation [8], discharge [9–15] and electron impact ionization [16]. Most of these techniques have shown that indeed intense beams of rotationally cold ions can be produced, but to date only Ar–HN$_2^+$ has been observed in a direct measurement using a slit

nozzle plasma [3]. The detection of rotational transitions involving the excitation of the C–O stretch in Ar–HCO$^+$ is presented here.

The vibration-rotation spectrum of Ar–HCO$^+$ has been observed in the C–H stretch (ν_1) region by mass selective infrared photodissociation experiments, yielding reasonably accurate molecular constants for the vibrational ground state [17]. These constants guided a search for pure rotational transitions of Ar–HCO$^+$ and three isotopomers – Ar–DCO$^+$, Ar–H^{13}CO$^+$, Ar–HC^{18}CO$^+$ – yielding molecular structure and values for the intermolecular vibrational motions [2]. Recently, ab initio correlated levels of theory have been employed on Ar–HCO$^+$, giving estimates for the induced red shifts of the free C–H and C–O stretches upon complexation [18].

2. Experiment

The experimental apparatus has been described [16]. The characteristics of the slit plasma have been discussed on the example of N$_4^+$ [19,20]. The spectrometer consists of a commercial tunable diode laser and a supersonic slit jet apparatus. The plasma is generated by electron impact ionization of a gas mixture that is expanded through a 32 mm × 50 μm slit. The planar jet is multipassed by the laser beam, increasing the total effective absorption pathlength to approximately 42 cm, and is subsequently monitored

by a quadrupole mass spectrometer. In Fig. 1 a typical mass spectrum for a Ar/H$_2$/CO mixture is shown, demonstrating the complex distribution of the generated species. Besides Ar–HCO$^+$ and the expected Ar$_n$H$_m^+$ species, more exotic complexes as (CO)$_2$H$^+$ and (CO)$_2$H$_3^+$ can be observed. Without H$_2$ in the expansion strong Ar-CO$^+$ and (CO)$_2^+$ signals are found. The number of neutral radicals and radical complexes will be of the same order of magnitude as the charged ones, but these are not monitored with the present setup. The average Ar–HCO$^+$ density in the zone probed by the infrared beam is estimated as 5–10 × 10^9 cm^{-3}.

The laser radiation is focussed onto an InSb detector and is phase-sensitively detected by production modulation at 5 kHz. An additional 5% band pass filter is used to suppress background radiation of the plasma. The spectra are calibrated by simultaneously recording marker etalons and N$_2$O or CO spectra as reference. In this way an absolute accuracy better than 0.002 cm^{-1} can be obtained.

The optimal production conditions for Ar–HCO$^+$ are found for a mixture of approximately 100:20:1 Ar, H$_2$, and CO and a stagnation pressure of about 2.5 bar. The rotational temperature is of the order of 20 to 30 K under these conditions. The effective measuring time is limited to typically 1 hour by the lifetime of the filament in the H$_2$/CO/Ar plasma, which complicates the scanning procedure.

3. Results and discussion

In total 34 adjacent vibration-rotation lines have been found that are assigned to the shifted C–O stretch of Ar–HCO$^+$. The spectrum shows the ordered structure of a Σ–Σ transition of a linear molecule, with P and R branch and a band gap of 4B. In Fig. 2 part of the infrared absorption spectrum is shown. The signal-to-noise ratio of the strongest transitions is ≈ 15. The line positions and rotational assignment are listed in Table 1. The exact determination of the P(3) transition is not possible due to a partial overlap with a CO absorption at 2135.31 cm^{-1}.

The assignment of the spectrum to Ar–HCO$^+$ is straightforward, although the method is not mass
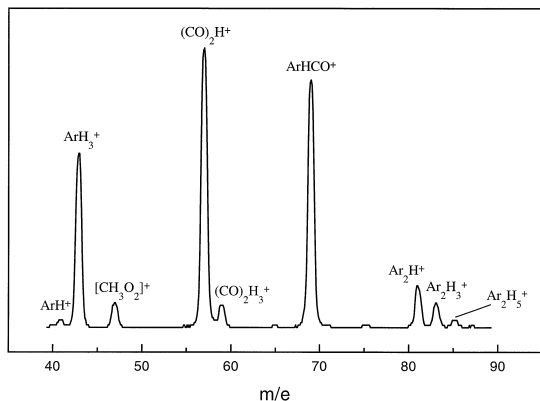

Fig. 1. The mass spectrum showing the ionic species produced in a slit expansion of Ar, H$_2$ and CO with electron impact ionization. The peak at 47 amu may be due to (CO)H$_3$O$^+$ or (H$_2$O)HCO$^+$.

Table 1
Observed frequencies (in cm^{-1}) of rotational transitions involving excitation of the C–O stretch in Ar–HCO^+. The obs. − calc. values are obtained, using the rotational parameters listed in Table 2

J	P-branch	obs. − calc. (10^{-4})	R-branch	obs. − calc. (10^{-4})
0			2135.8419	10
1	2135.5750	5	2135.9754	2
2	2135.4421	−2	2136.1106	5
3	–		2136.2464	6
4	2135.1808	7	2136.3837	15
5	2135.0522	21	2136.5197	5
6	2134.9221	14	2136.6563	−7
7	2134.7934	13	2136.7952	−2
8	2134.6650	8	2136.9340	−6
9	2134.5373	3	2137.0731	−13
10	2134.4103	−3	2137.2129	−20
11	2134.2846	−2	2137.3541	−20
12	2134.1588	−10	2137.4955	−25
13	2134.0341	−14	2137.6386	−20
14			2137.7823	−15
15			2137.9280	3
16			2138.0749	26
17			2138.2150	−26
18			2138.3618	−17
19			2138.5107	5
20			2138.6592	17
21			2138.8089	35

Fig. 2. The R(16) to R(18) absorption signals of the $\nu_3 = 1 \leftarrow v = 0$ transition of Ar–HCO^+ observed in a slit nozzle expansion with electron impact ionization. The signals are recorded in direct absorption, employing production modulation.

selective and many different species are formed in the plasma. The absorption signals are not observed without Ar or H_2 or CO in the expansion and scale with the Ar–HCO^+ mass signal. Because both P- and R-branch transitions have been measured, combination differences can be calculated yielding values for the ground state rotational progression. These agree within the experimental uncertainty with the values calculated from the constants determined by microwave spectroscopy for Ar–HCO^+ [2].

The observed transitions of the ν_3 band of Ar–HCO^+ have been analyzed, assuming a pseudo-diatomic energy level expression for the gro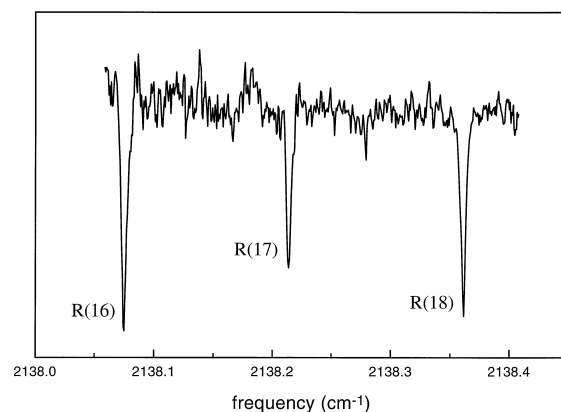und and excited states, with the rotational energy levels expressed as an expansion in $J(J + 1)$. Subsequently, the P and R branch line positions were fitted with B'' and D'' constrained to the values determined in the microwave experiment [2]. The values of the band origin and excited state constants are fitted to within the experimental accuracy with the expansion terminated at the second term. While the B' value is determined to an accuracy better than 0.05%, the uncertainty in an unrealistic small D' value is larger than the fitted constant itself, and hence is not a meaningful physical parameter. As has been observed for other ion complexes, this is due to the relatively strong bonds which make distortional effects visible only for highly excited rotational states [3]. These states are not sufficiently populated in the jet expansion to be visible. Therefore D' was kept fixed to the ground state value, which makes the overall accuracy of the fit worse, yielding some obs. − calc. differences (Table 1) that are slightly larger than the experimental uncertainty. As is observed for ν_1 excited transitions in the infrared predissociation spectrum (unpublished results from this laboratory), a weak perturbation in the upper

Table 2
Spectroscopic constants (in cm^{-1}) determined for the $\nu_3 = 1$ level of Ar–HCO^+. The ground state values given for comparison are from the microwave study [2]

$v = 0$	0	$B'' = 0.066431978(5)$	$D'' = 6.534(5) \cdot 10^{-8}$
$\nu_3 = 1$	$\nu_0 = 2135.7073(4)$	$B' = 0.0667835(18)$	$D' = D''$

state may be involved as well, which could explain the non-systematic behaviour of the deviations. The derived constants are listed in Table 2.

Neglecting zero point vibration and assuming an undistorted HCO^+ unit, an Ar–H separation of 2.125 Å is calculated in the excited state using the rotational parameters derived here and the values listed in [18,21]. This is approximately 0.01 Å shorter than the ground state value [2], but about 0.04 Å longer as the proton-argon separation found on excitation of the C–H stretch [17]. This may be expected because the C–O stretch is not directly involved in the intermolecular bond, as is the case for the C–H stretch. Consequently, the red shift that is induced upon complexation is expected to be smaller for the excited ν_3 vibration as well.

The ν_3 band origin is found at 2135.7073(4) cm^{-1}, red shifted by 48.24 cm^{-1} compared to the C–O stretch in free HCO^+ [21]. This value is large compared to shifts in neutral systems involving rare-gas atoms complexed with small molecules. Vibrational shifts of just a few wavenumbers are the rule there. The effect is even more striking for the excited C–H stretch, where a red shift of 274 cm^{-1} has been found [17]. This has been explained by the fact that the proton is attracted both by the CO and Ar, reducing the characteristic frequency for its motion. Although the C–O stretch is not directly involved in the intermolecular bond, the shift is still remarkably large.

In a Post-Hartree–Fock study on $Ar–HCO^+$ (and $He–HCO^+$) rotational constants, harmonic vibrational frequencies and absolute infrared intensities have been calculated [18]. The magnitude of the red shift for the C–H stretching vibrational band upon complex formation is closely reproduced ($\Delta\nu_{exp} = 274$ cm^{-1} versus $\Delta\nu_{theor} = 254.8$ to 272.5 cm^{-1}). The shift of the C–O stretch is calculated to be 30.7 to 40.7 cm^{-1}, depending on the method used, which is in accord with the 48.24 cm^{-1} shift observed experimentally here. In Ref. [18] it is argued that the interpretation of the rovibrational spectra of He–HCO^+ [17] gives a too large value for the He–H distance due to dynamical effects in the complex. This is also known from the extensive work on neutral complexes, where the outcome of experiments, probing an averaged structure, does not agree with the conclusions of ab initio optimizations that

directly provide the minimum energy configuration. In the case of He–HCO^+ this effect is discussed in a recent comment by explicitly taking into account zero point effects [22]. The discussion may benefit from results of the excited C–O stretch in He–HCO^+, as dynamical effects are expected to be less prominent in this case.

Harmonic frequencies of $\nu_s = 131$ cm^{-1} and $\nu_b = 109$ cm^{-1} have been calculated for Ar–HCO^+ from the intermolecular stretching and bending force constants [2]. Consequently, the $(\nu_3 + \nu_s)$ and $(\nu_3 + \nu_b)$ combination bands are expected in the 2220 to 2280 cm^{-1} range. The first attempts to observe these bands have failed, presumably of the much weaker intensities of the combination bands [2].

The transitions observed in the slit nozzle plasma are nearly Doppler free because the expansion has no velocity component in the direction of the laser beam. The 120 MHz linewidth is caused mainly by the bandwidth of the laser and residual broadening in the multipass system. This puts a rough lower limit of 1.3 ns on the lifetime of the Ar–HCO^+ in the $\nu_3 = 1$ excited vibrational level.

4. Conclusion

The Ar–HCO^+ ionic complex has been studied in a direct absorption measurement using a slit nozzle expansion with electron impact ionization. The transitions involving the excitation of the ν_3 vibration have been observed at rotational resolution and the spectrum shows that the complex has a linear equilibrium structure. The ν_3 vibrational red shift of 48.24 cm^{-1} upon complexation indicates that the coupling of the C–O stretch to the intermolecular bond is still considerable.

Acknowledgements

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