Millimetre-Wave and Submillimetre-Wave Spectroscopy of Molecular Ions [and Discussion]

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Millimetre-wave and submillimetre-wave spectroscopy of molecular ions

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In the last few years, the specificities of millimetre-wave spectroscopy coupled with active developments in other fields (*ab initio* calculation, radioastronomy and infrared spectroscopy) have led to an impressive increase in our knowledge of the spectral characteristics of molecular ions. The advances to be reviewed in this paper are a result of the development of highly sensitive spectrometers and of efficient methods of production. Some specific examples, including ions with large-amplitude motion (H_3O^+), weakly polar ions ($HCNH^+$), asymmetric-top ions (HCO_2^+, HON_2^+) and ionic clusters ($Ar{\cdot}H_3^+$), will be used to illustrate the potentialities of millimetre- and submillimetre-wave spectroscopy.

1. Introduction

The exciting story of high-resolution rotational spectroscopy of molecular ions began in 1970 with the discovery of the so-called X-ogen interstellar line by Buhl & Snyder (1970) and the subsequent proposal by Klemperer (1970) that this line was caused by the HCO^+ ion. This identification, strongly supported by *ab initio* calculations (Wahlgreen *et al.* 1973; Kramers & Diercksen 1976) and by the observation of an interstellar line attributed to the ^{13}C substitution (Snyder *et al.* 1976), became definitive with the laboratory detection of HCO^+ in a glow discharge by Woods & co-workers (Woods *et al.* 1975). HCO^+ has been the first example of a remarkably fruitful approach with radioastronomical results, *ab initio* calculations and laboratory measurements. HN_2^+, HCS^+, HCO_2^+ have been also first observed in the interstellar medium (Turner 1974; Green *et al.* 1974; Thaddeus *et al.* 1981) before being detected in the laboratory (Saykally *et al.* 1976*a*; Gudeman *et al.* 1981; Bogey *et al.* 1984*b*). The discovery of the key role played by ions in interstellar chemistry has been indeed very stimulating for radioastronomers, theoreticians, and laboratory spectroscopists: more than 40 ions are now characterized by their millimetre spectra and/or infrared (IR) spectra.

In addition to its significance for astrophysics, millimetre-wave spectroscopy also gives essential information about energy-level configurations and molecular structure. Millimetre-wave spectroscopy, because of its frequency range, is inherently a very high-resolution technique (typically of the order of 100 kHz) and makes possible a detailed analysis of the rotational, fine and hyperfine structures and leads to an accurate determination of the molecular parameters.

During the last few years, these advantages have been shared with tunable IR spectroscopy. As these aspects are described in detail in other papers at this symposium, we will restrict ourselves to the methods and contributions of millimetre- and submillimetre-wave spectroscopy with tunable sources. We will consider first the highly sensitive spectrometers needed to observe molecular ions and then the efficient methods of ion production developed in different groups. Finally, we will illustrate the power of millimetre-wave spectroscopy by describing some recent results we obtained in Lille.

2. Millimetre and submillimetre spectrometers

With the exception of a few promising experiments with molecular beams (Brown *et al.* 1981; Johnson *et al.* 1984) that will not be described here, molecular ions are generally produced and observed inside low-pressure plasmas. Even with optimized methods of production, the ion density is always very weak, and the main quality required of a spectrometer is a detection threshold as low as possible. Considering a linear molecule as an example, the lowest detectable concentration $N_{\min}$ (per cubic centimetre) is given by the following expression:

$$N_{\min} \approx 6.56 \times 10^{27} \frac{T^2 \Delta\nu \gamma_{\min}}{\mu^2 \nu_0^3} \mathrm{e}^{W/0.69T},$$

where T is the temperature of the gas, assuming thermal equilibrium, in kelvins; $\Delta\nu$ is the half width at half maximum, in megahertz; $\gamma_{\min}$ is the minimum detectable absorption coefficient, in reciprocal centimetres; μ is the dipole moment, in debyes†; ν_0 is the frequency of the line, in megahertz; and W is the energy of the lower level of the transition, in reciprocal centimetres.

As illustrated in table 1, it is clear that two parameters can play a favourable role.

Table 1. Lowest detectable concentration, $N_{\min}$, calculated for some typical conditions assuming a spectrometer sensitivity of 10^{-7} cm^{-1}

μ/D	ν/GHz	T/K	$N_{\min}$/cm^{-3}	example
1.8	128	300	3×10^9	HCS^+
3.8	90	100	4×10^8	HCO^+
3.8	360	100	8×10^6	
0.5	370	200	7×10^8	$HCNH^+$

1. Cooling the cell increases the absorption coefficient and has often proved to be very effective (sometimes necessary) (Dixons & Woods 1975). Nevertheless, when condensable chemicals are involved in the gas mixture, only moderate cooling can be used, and no gain is to be expected from this parameter (Gudeman *et al.* 1981; Bogey *et al.* 1985*a*).

2. Working in a higher-frequency range permits the detection of weaker ionic concentrations, provided that the sensitivity of the spectrometer is the same as at lower frequencies. In the millimetre range (*ca.* 100–150 GHz) a typical value $\gamma_{\min} \approx 10^{-7}$ cm^{-1} can be obtained for the lowest detectable absorption coefficient in a routine experiment. This moderate sensitivity is mainly because of specific constraints related to discharges such as relatively short cells and discharge instabilities. Such a sensitivity is nevertheless difficult to reach in the submillimetre-wave range if harmonic generation from low-frequency klystrons is used, because of the lower power available. But with a relatively powerful radiation source, detection thresholds as low as those shown in table 1 can be achieved and the detection of minor ionic species in the discharge is possible.

In the millimetre-wave range, fundamental klystrons are currently available up to about 120 GHz. Although klystrons are also used at higher frequencies (Saito *et al.* 1985), generally, radiation in the 120–300 GHz range is obtained by harmonic generation by using point contact or Schottky barrier diodes. Depending on the frequency range, point contact, Schottky barrier diodes or liquid-helium-colled InSb bolometers have been used as detectors.

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† 1 D ≈ 3.33×10^{-30} C m.

The spectrometer developed in Lille is of conventional design and has been described elsewhere (Bogey *et al.* 1986*c*). Varian klystrons ($f < 80$ GHz) are phase locked to a solid-state oscillator driven by a synthesizer (ADRET 6100 B). A 12.5 kHz frequency modulation is applied to the klystron by modulating the reference frequency of the phase-lock synchronizer. Above 120 GHz, the millimetre-wave power is obtained by harmonic generation by using Schottky barrier diodes mounted in commercial Custom Microwave multipliers, and detection is achieved with an InSb detector (IRD4 Advanced Kinetics) operating at 4 K. After synchronous detection, the signal is processed by a microprocessor system that ensures, in addition to the control of the frequency scans, multichannel averaging, base-line suppression, signal smoothing and line-centre frequency measurement, the later being achieved by taking the mean value of increasing and decreasing frequency scans (Bogey *et al.* 1986*c*).

In the submillimetre-range, harmonic generation is often used (Sastry *et al.* 1981; Verma *et al.* 1985; Bogey *et al.* 1986*f*). For the study of unstable species, which requires high sensitivity, this technique is generally limited to about 500 GHz, and other methods have been developed for frequencies in the terahertz region or above. Tunable far-infrared radiation has been generated by mixing the radiation of submillimetre-wave lasers with that of a klystron by using Schottky barrier diodes (Van den Heuvel *et al.* 1980; Blake *et al.* 1986; Laughlin *et al.* 1986), or by mixing two CO_2 laser lines in metal–insulator–metal diodes (Evenson *et al.* 1984).

In Lille, we use a backward wave oscillator (Thomson C.S.F. TH 4218 D) that delivers at least 10 mW in the 330–406 GHz frequency range.

The short-term frequency stability is adequate to use the carcinotron in a free running mode. Figure 1*a* presents a recording of the 1_{11}–1_{10} transition of H_2D^+ (Bogey *et al.* 1984*a*) with this technique. This is a considerable bonus when searching for a new molecule with a large uncertainty on the line frequencies because, in these conditions, a very large frequency range can easily be scanned (up to 40 GHz continuously, such as in the case of $Ar \cdot D_3^+$, to be discussed

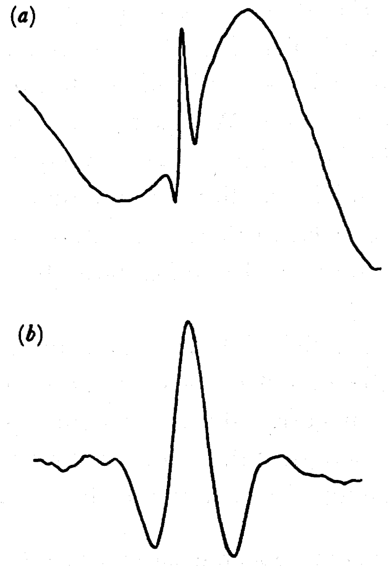

FIGURE 1. Two examples of the use of the backward wave oscillator in the submillimetre-wave range. (*a*) Free-running mode for the 1_{11}–1_{10} H_2D^+ line near 372 GHz. Lock-in time constant = 100 ms; the width of the region shown is 16 MHz and the sweeping time is about 30 s. The crooked base line is because of standing waves in the cell. (*b*) Phase-locked mode for the $J = 5 \leftarrow 4$ transition of $HCNH^+$ at about 370 GHz. Lock-in time constant = 10 ms; the signal has been averaged 120 times.

later). When signal averaging is required, the carcinotron is phase locked (Bogey *et al.* 1986*b*). A part of the submillimetre radiation is extracted with a beam splitter and mixed on a Schottky diode with the harmonics of phase-locked millimetre-wave klystron radiation. The microprocessor system that drives the millimetre-wave spectrometer described above can then be used to control the submillimetre spectrometer, leading to a significant improvement in the sensitivity. This technique allows the detection of very weak signals arising, for example, from weakly polar molecules such as $HCNH^+$, as illustrated in figure 1*b*.

As a check of the sensitivity of the spectrometer the $J = 30 \leftarrow 29$ transition of OCS in the $(10^0\,1)$ vibrational state has been observed at 361572.17 MHz with a signal:noise ratio of two in a single scan with a lock-in time constant of 30 ms, corresponding to a minimum detectable absorption coefficient of 5×10^{-8} cm^{-1} in this frequency range.

3. Methods of production

In spite of the unrecognized pioneering work of Low & Ramberg (1955), who in 1955 observed OH Λ doubling transitions inside a DC discharge, the noise generated by the plasma electrons had been thought for a long time to prevent the possibility of observing millimetre-wave spectra in an internal discharge. In 1974, however, Woods & co-workers demonstrated that this technique was very promising by observing some transient molecules inside a DC glow discharge (Woods & Dixon 1974). They succeeded in detecting the first laboratory rotational spectrum of a molecular ion, CO^+ (Dixon & Woods 1975).

The characteristics of a glow discharge depend on various parameters such as the nature and pressure of the gas, and the shape of the electrodes (Badareu & Popescu 1968; Von Engel 1965). In fact, the discharge is not spatially homogeneous and two parts of a glow discharge have characteristics compatible with the requirements of millimetre-wave spectroscopy, i.e. mainly a low and homogeneous electric field.

1. The *positive column* is characterized by a moderate (less than 10 V cm^{-1}) and uniform electric field. This macroscopic electric field induces a weak Doppler shift on the absorption frequencies of the molecular ions and can be used to discriminate these lines from those originating from neutrals (Gudeman 1982; Woods 1983). This phenomenon is the basis of the very efficient velocity-modulation technique extensively used in the IR spectral range (Gudeman & Saykally 1984), in which the direct interaction between the radiation and the plasma is negligible. Although the electron density is relatively low (*ca.* 10^9–10^{10} cm^{-3}), the column density in the positive column can be rather large because it fills the largest part of the discharge tube.

2. In the *negative glow*, the electric field is very weak and the Doppler shift is negligible (Bowman *et al.* 1982). Moreover, the ionic density is about one order of magnitude higher than in the positive column, making the negative glow very attractive for absorption spectroscopy. However, in normal conditions, the length of the negative glow is very small (a few centimetres) and special devices have to be developed to lengthen it for use in absorption spectroscopy.

3.1. *Millimetre-wave spectroscopy in the positive column*

The earliest microwave observations inside a low-pressure plasma took place in the positive column of a DC discharge (Low & Ramberg 1955; Woods & Dixon 1974; Dixon & Woods 1975) and a number of molecular ions have now been detected by this technique (Sastry *et al.*

1981; Woods 1983). This technique is also very efficient for the production of free radicals (Dixon & Woods 1977; Hirota 1985), metastable species (Saykally *et al.* 1976*b*; Saykally 1977), unstable molecules (Thaddeus *et al.* 1986; Tang *et al.* 1985) as well as vibrationally excited species (Saykally 1977; Skatrud *et al.* 1983; Gudeman 1982). Although the positive column has been used very successfully in the study of elusive molecules, some problems occasionally arise from the presence of metal electrodes inside a very reactive plasma (Woods & Dixon 1974; Saykally *et al.* 1976*a*). In Lille we have developed an electrodeless radiofrequency discharge that avoids these problems (Bustreel *et al.* 1979; Bogey *et al.* 1981) and has plasma characteristics very similar to those of a positive column. Figure 2 illustrates the absorption cell, 1 m long with an internal diameter of 5 cm with cooling possible to liquid-nitrogen temperature. The plasma is excited by an RF oscillator delivering up to 1 kW of power at 50 MHz. About 50% of the power is coupled to the gas, and corresponds to a power density as high as 0.25 W cm^{-3}. Such high power is not necessary for the simple protonation of a stable molecule (Bogey *et al.* 1981) but is required to induce the relatively complex reactions that produce HCS$^+$ (Bogey *et al.* 1984*c*) or to populate highly excited vibrational states of neutrals (Bogey *et al.* 1982*a*, *b*, 1986*c*, *d*; Anacona *et al.* 1986) or ions (Bogey *et al.* 1983). Table 2 summarizes these results. Relative intensities of rotational transitions in successive vibrational states correspond to vibrational temperatures in the range 2000–4000 K, depending on the

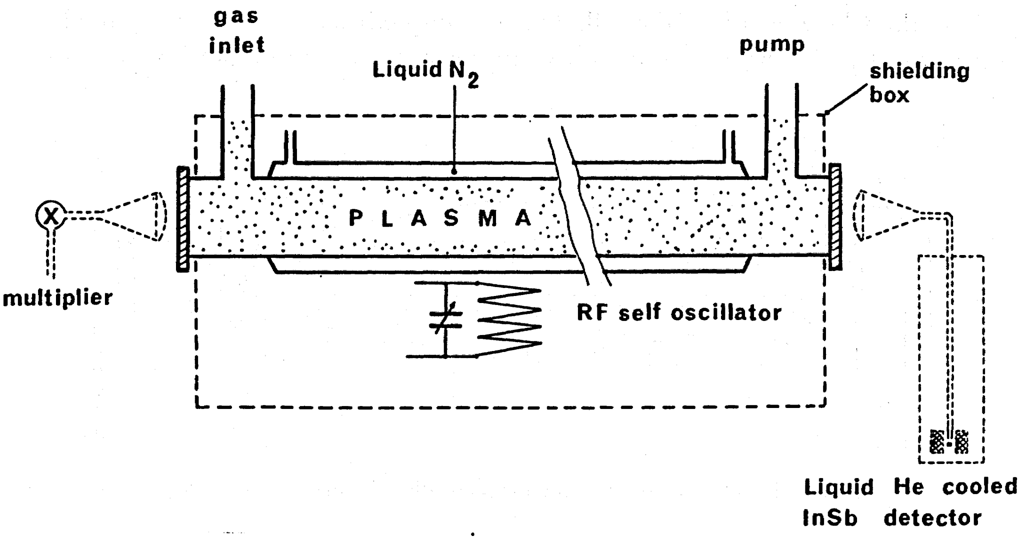

FIGURE 2. Schematic diagram of the radiofrequency (RF) discharge cell.

TABLE 2. DIATOMIC MOLECULES OBSERVED BY MILLIMETRE-WAVE SPECTROSCOPY IN VIBRATIONALLY EXCITED STATES

	$v_{\max}$	E_v/cm^{-1}	$E_{\mathrm{dissociation}}/\mathrm{cm}^{-1}$	references
CO	40	66000	90000	Bogey *et al.* (1986*c*)
CS	20	23500	59000	Bogey *et al.* (1982*b*)
CN	9	18500	63000	Bogey *et al.* (1986*d*)
SO	8	9500	27000	Bogey *et al.* (1982*a*)
NS	5	6500	39000	Anacona *et al.* (1986)
CO$^+$	4	9500	67000	Bogey *et al.* (1983)

species of interest. From measurements of the plasma refractive index, the electron density has been estimated to be about 10^{10} cm^{-3}, which is of the same order of magnitude as in a positive column (Woods 1983).

3.2. *Spectroscopy in the negative glow*

As previously mentioned, the main attractive point of the negative glow, which develops near the cathode, is the high density of the plasma. Two discharges, the hollow cathode, and the magnetically confined glow, have been designed to lengthen the negative glow of a DC discharge.

In the hollow cathode, the primary electrons form an axial beam that enhances the ion density along the whole length of the cell. This technique has been extensively used in optical spectroscopy for a very long time but its first application to submillimetre-wave spectroscopy

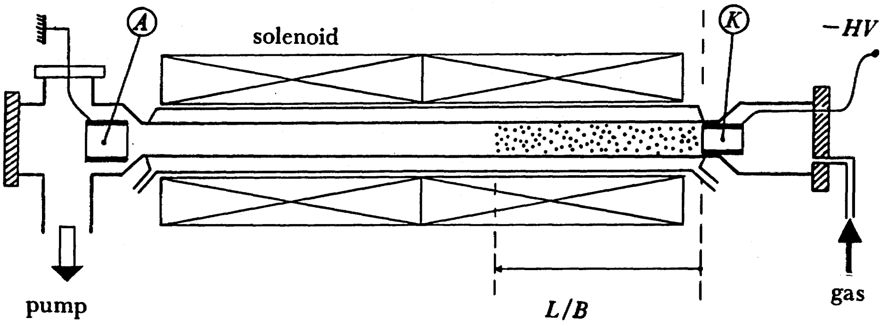

FIGURE 3. Schematic diagram of the magnetically confined negative glow discharge.

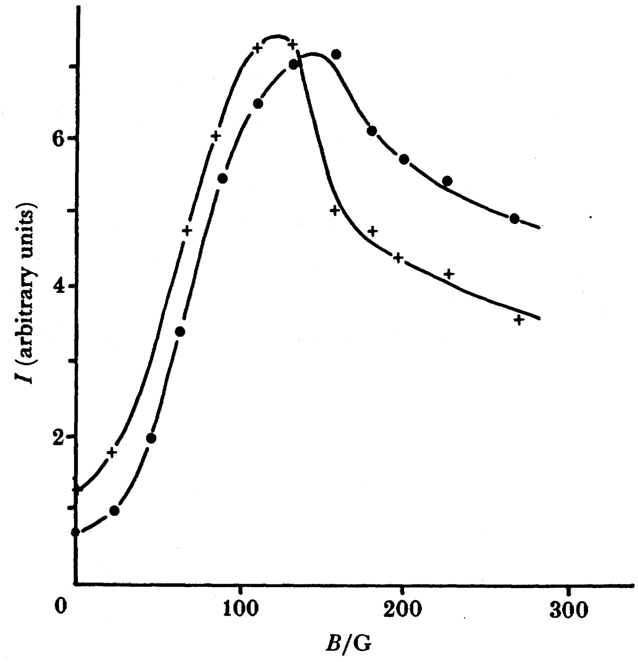

FIGURE 4. Characteristic variation of ionic line intensity against the confinement magnetic field. Symbols: ●, H_2D^+; +, $Ar{\cdot}H_3^+$. (1 G = 10^{-4} T.)

TABLE 3. MOLECULAR IONS OBSERVED BY TUNABLE MILLIMETRE- AND SUBMILLIMETRE-WAVE SPECTROSCOPY

ions	isotopes	methods of production	frequency range/GHz	experimental techniques	other methods	references to the first laboratory observation
CO^+	^{13}C, ^{18}O	PC, RF	118–1061	K, HG, SBL	IR, OPT	Dixon & Woods (1975)
HCO^+	D, ^{13}C, ^{18}O	PC, RF, HC	89–1070	K, HG, SBL	IR, IS	Woods *et al.* (1975)
HN_2^+	D, ^{15}N	PC, HC	90–1024	K, HG, SBL	IR, IS	Saykally *et al.* (1976*a*)
HCS^+	—	PC, RF	85–299	K, HG	IR, IS	Gudeman *et al.* (1981)
HOC^+	D, ^{18}O, ^{13}C	PC, MC	89–382	K, HG, BWO	IR	Gudeman & Woods (1982)
NO^+	—	MC	238–358	HG	OPT	Bowman *et al.* (1982)
ArH^+	D	MC	317–634	HG, SBL	IR	Bowman *et al.* (1983)
KrD^+	—	MC	252	HG	IR	Warner *et al.* (1984*a*)
H_2D^+	—	MC, HC	156–372	K, HG, BWO	IR, IS?	Bogey *et al.* (1984*a*); Warner *et al.* (1984*b*)
HCO_2^+	D	MC	340–405	BWO	IR, IS	Bogey *et al.* (1984*b*)
H_3O^+	—	MC	307–396	HG, BWO	IR, IS?	Bogey *et al.* (1985*a*); Plummer *et al.* (1985)
SO^+	—	DC, MC	69–250	K, HG	OPT	Warner *et al.* (1985)
$HCNH^+$	D	MC	148–370	HG, BWO	IR, IS	Bogey *et al.* (1985*b*)
OH^+	D	HC	909–1045	SBL	OPT, IR	Bekoy *et al.* (1985)
HON_2^+	D	MC	134–405	HG, BWO	IR	Bogey *et al.* (1986*e*)
NH^+	—	HC	1020	SBL	OPT	Verhoeve *et al.* (1986*b*)
CF^+	—	MC	102–410	HG	IR	Plummer *et al.* (1986)
HBF^+	D, ^{10}B	MC	145–363	HG	IR	Cazzoli *et al.* (1986)
ArH_3^+	D	MC	182–392	HG, BWO		Bogey *et al.* (1987)

Abbreviations: PC, positive column discharge; RF, radiofrequency discharge; HC, hollow-cathode discharge; MC, magnetically confined negative glow discharge; K, fundamental klystron; HG, harmonic generation; SBL, tunable side-band laser; BWO, backward wave oscillator; IR, infrared spectroscopy; OPT, optical spectroscopy; IS, interstellar detection.

is by Van den Heuvel & Dymanus (1982) who first observed rotational transitions of ions in the terahertz region. This device has been now used to study some light ions such as OH^+ (Bekooy *et al.* 1985), OD^+ (Verhoeve *et al.* 1986*a*), NH^+ (Verhoeve *et al.* 1986*b*), and ArH^+ (Laughlin *et al.* 1986). A similar device allowed Saito *et al.* (1985) to observe a millimetre-wave transition of H_2D^+.

In the magnetically lengthened negative glow, first developed by De Lucia & co-workers (1983), an axial magnetic field is used to confine the primary electrons and to limit ambipolar diffusion to the walls. The diagram, of the cell built in Lille is presented in figure 3. A magnetic field of about 200 G is generally sufficient to lengthen the negative glow to the 1 m length of our discharge cell. The discharge conditions correspond to those of the anormal glow discharge, i.e. high voltage across the discharge (2–5 kV) and low current (1–10 mA). Traces of reactant gases (10^{-4}–10^{-3} Torr†) are mixed with Ar used as a buffer gas, and the total pressure is generally lower than 10 mTorr. A variation of the intensity of an ion line with the confining magnetic field B is very characteristic: namely, a sharp initial increase with B, and the existence of an optimum magnetic field. This very typical behaviour is illustrated in figure 4, which shows the H_2D^+ line intensity dependence on the strength of the magnetic field. Such behaviour can be used to discriminate ion lines from neutral ones. The second curve in figure 4 definitely demonstrates that the line studied (unidentified at that time) could be ascribed to an ionic species, later identified as the ionic complex $Ar{\cdot}H_3^+$, as will be described in a following section.

This technique has proved to be very efficient, leading to the discovery of a variety of new ions in the last five years, from ions with very small dipole moments, NO^+ (Bowman *et al.* 1982), H_2D^+ (Warner *et al.* 1984*b*; Bogey *et al.* 1984*a*), to the first asymmetric tops, HCO_2^+ (Bogey *et al.* 1984*b*, 1986*b*), HON_2^+ (Bogey *et al.* 1986*e*) or $Ar{\cdot}H_3^+$ (Bogey *et al.* 1987).

To conclude this section, table 3 summarizes the ions so far detected by tunable millimetre- and/or submillimetre-wave spectroscopy.

4. SPECTROSCOPIC STUDIES OF INDIVIDUAL IONIC SPECIES

The highly sensitive spectrometers and efficient methods of production described above have enabled us to detect many molecular ions, and we will consider in this section some examples that are characteristic of the specific problems encountered in these studies.

4.1. *An ion with large amplitude motion:* H_3O^+

This ion is one of the most fundamental molecular ions because of its important role in various physical–chemical processes reaching from biological systems (Eigen 1964) to interstellar clouds (Leung *et al.* 1984; Viala 1986). This ion is isoelectronic with NH_3 and has the same well-known umbrella shape, with a double minimum potential leading to an inversion splitting of the energy levels. Earliest theoretical calculations of the ground-state inversion splitting ranged from 28 to 72 cm^{-1} (Spirko & Bunker 1982; Botschwina *et al.* 1983; Bunker *et al.* 1983, 1984) making the prediction of the inversion rotation spectrum of this ion impossible. High-resolution IR spectra of H_3O^+ observed by different groups (Begeman *et al.* 1983; Haese & Oka 1984; Lemoine & Destombes 1984; Davies *et al.* 1985; Liu *et al.* 1985; Liu & Oka 1985) have

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† 1 Torr ≈ 133.3 Pa.

indicated the frequency range where its inversion spectrum can be expected. Fortunately, the three $K = 0, 1, 2$ components of the $J = 3^+ \leftarrow 2^-$ were predicted to lie in the frequency range covered by our carcinotron and the search of these lines has been greatly facilitated by the good spectral purity and stability of the carcinotron used in the free running mode.

Three lines have been observed in the magnetically confined negative glow discharge in a mixture of H_2O (10^{-4} Torr), H_2 (4×10^{-4} Torr), and Ar (15×10^{-3} Torr) at room temperature, and have exhibited the typical intensity variation against the confining magnetic field expected for ion lines. This is well illustrated in figure 5. The three frequencies were well within the uncertainties given by Liu & Oka (1985) and their assignment to H_3O^+ lines has been confirmed by chemical evidence (Bogey *et al.* 1985*a*). At the same time the $J, K = 1^-, 1 \leftarrow 2^+, 1$ line was observed by Plummer *et al.* (1985) in similar experimental conditions. These four lines, although accurately measured, permitted only the determination of a linear combination of various molecular parameters. Then, a global fit of both submillimetre and IR data led to a significant improvement of the molecular constant determination (Liu *et al.* 1986).

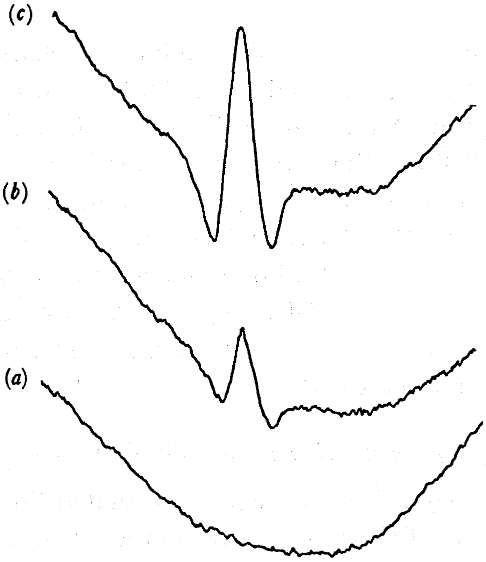

FIGURE 5. Evolution of the $J, K = 3^+, 0 \leftarrow 2^-, 0$ transition of H_3O^+ against magnetic field (396272.412 MHz). The discharge current has been kept constant at $I = 4$ mA; $p_{H_2O} = 10^{-4}$ Torr; $p_{H_2} = 4 \times 10^{-4}$ Torr; $p_{Ar} = 15 \times 10^{-3}$ Torr. Lock-in time constant = 100 ms. The width of the region shown is about 8 MHz. (*a*) 0 G; (*b*) 75 G; (*c*) 150 G.

The $J, K = 1^-, 1 \leftarrow 2^+, 1$ transition, which connects relatively low-lying energy levels, has been tentatively detected in two astronomical sources (Wootten *et al.* 1986; Hollis *et al.* 1986). The observation of the $J = 3^+ \leftarrow 2^-$ components would confirm this identification and would place H_3O^+ among the most abundant molecular ions in the interstellar gas, in agreement with theoretical predictions (Leung *et al.* 1984; Viala 1986).

4.2. *A weakly polar ion:* HCNH$^+$

Although it is much less stable than HCN in laboratory conditions, the isomer HNC has been detected in several interstellar sources with an abundance comparable to that of HCN. This is strong support for a production mechanism involving dissociative recombination of the protonated molecule $HCNH^+$ (Leung *et al.* 1984). In view of its importance in astrochemistry, this ion has been the subject of numerous *ab initio* calculations to provide accurate rotational frequencies (Allen *et al.* 1980; Haese & Woods 1979; Dardi & Dykstra 1980). However, because of the small calculated dipole moment (0.3 D or less) (Haese & Woods 1979; Dardi & Dykstra 1980; Lee & Schaefer 1984), its detection by millimetre-wave spectroscopy was expected to be difficult. Although ions generally have a rather large dipole moment, some weakly polar ions have also been observed (NO^+, Bowman *et al.* 1982; H_2D^+, Bogey *et al.* 1984*a*; Warner *et al.* 1984*b*; Saito *et al.* 1985). For $HCNH^+$, IR detection (Altman *et al.* 1984*a*, *b*; Amano 1984) has provided accurate rotational parameters that facilitated the submillimetre search.

First observations were made in a magnetically confined discharge through a mixture of HCN (8×10^{-4} Torr), H_2 (6×10^{-3} Torr) and Ar (15×10^{-3} Torr) cooled to 220 K. The discharge conditions were typical of those needed for the observation of ions ($I = 2$ mA; $HV = 2200$ V; optimum $B = 200$ G). Subsequently, it was found that an improvement of about 5 in the signal:noise ratio could be obtained at liquid-nitrogen temperature by discharging a mixture of CH_4 (1.5×10^{-3} Torr) and N_2 (18×10^{-3} Torr). By using harmonic generation, two more lines were observed, leading to an accurate determination of the B and D values in very good agreement with IR results (Bogey *et al.* 1985*b*). Both IR and millimetre-wave data finally led to accurate frequencies and to subsequent detection of $HCNH^+$ in the interstellar medium (Ziurys & Turner 1986).

4.3. *Slightly asymmetric-top ions:* $HOCO^+$, HON_2^+

In 1981, Thaddeus *et al.* detected three harmonically related lines in Sagr. B2 that were interpreted as $K = 0$ components of three successive rotational transitions of a nearly linear molecule. By comparing the deduced B value with *ab initio* calculations for a number of plausible molecules, they concluded that the most likely candidates for these lines were isoelectronic molecules, the protonated carbon dioxide $HOCO^+$ and the cyanic acid HOCN. The most conclusive way to solve this problem was to observe one or the other species in the laboratory. In a first step, we observed six lines in the 350–380 GHz range by discharging a mixture of CO_2 (2×10^{-5} Torr), H_2 (10^{-4} Torr) and Ar (6×10^{-3} Torr) slightly cooled by flowing cold N_2 gas around the cell. These lines were identified as the $K = 0$ and $K = 2$ components of the $J = 16 \leftarrow 15$ and $J = 17 \leftarrow 16$ transitions of $HOCO^+$. They fitted very nicely with the three astrophysical lines, giving a definite identification of the astrophysical carrier.

With the phase-locked carcinotron, a more extensive study of the spectrum has been carried out and higher K components have been observed in the same frequency range. By replacing H_2 by D_2 in the discharge, we have also been able to measure a number of transitions of $DOCO^+$ (Bogey *et al.* 1986*b*). At the same time, the first IR spectra were obtained by Amano & Tanaka (1985) with a hollow cathode discharge.

Protonated carbon dioxide is a very slightly asymmetric prolate rotor ($\kappa = -0.9996$) and because of the large value of the rotational constant A, only two different types of transitions can be observed in the frequency range of our submillimetre-wave source: a-type R-branch and b-type P- or R-branch transitions. Currently, only a-type ${}^{q}R_{K_a}$ transitions have been observed. They are characterized by $15 \leqslant J \leqslant 18$, $K_a \leqslant 5$ for $HOCO^+$ (29 lines) and $16 \leqslant J \leqslant 19$, $K_a \leqslant 6$ for $DOCO^+$ (31 lines). They have been fitted by using extended Watson's S-reduced hamiltonian in the I^r-axis representation, and a set of accurate molecular parameters has been determined that agrees with the predictions of *ab initio* calculations

(De Frees *et al.* 1982; Frisch *et al.* 1985) (table 4). A comparison of theoretical and experimental values permits the improvement of the prediction of the molecular constants of the ^{13}C isotopic species, which will be searched for in our laboratory in the near future.

According to *ab initio* calculations, the isoelectronic molecule HON_2^+ has a similar structure, i.e. a nearly linear backbone with the hydrogen slightly off axis, and the preferred site of protonation is the oxygen atom. However, the nitrogen-protonated form is predicted to be also stable and about 11.5 kcal mol^{-1}† above the oxygen-protonated form (Rice *et al.* 1986; Yamashita & Morokuma 1986; Vincent & Hillier 1986). Recently, Amano (1986) has measured the ν_1 IR band and has deduced molecular constants in agreement with those of the O-protonated form, permitting us to search for its rotational spectrum in the submillimetre-wave range.

Relatively strong lines belonging to a-type ^qR- and b-type ^rR-, ^qR- and ^rP-branches were observed in a mixture of N_2O (2×10^{-3} Torr), H_2 (7×10^{-3} Torr) and Ar (9×10^{-3} Torr). The optimum discharge conditions were $I = 5$ mA, $HV = 1600$ V, $B = 250$ G (Bogey *et al.* 1986*e*). By replacing H_2 with D_2, the DON_2^+ lines were easily found by using the carcinotron in the free running mode. Figure 6 illustrates the main advantage of this submillimetre source that enabled us to have an overview of the spectrum with a high sensitivity permitting the straightforward identification of the lines.

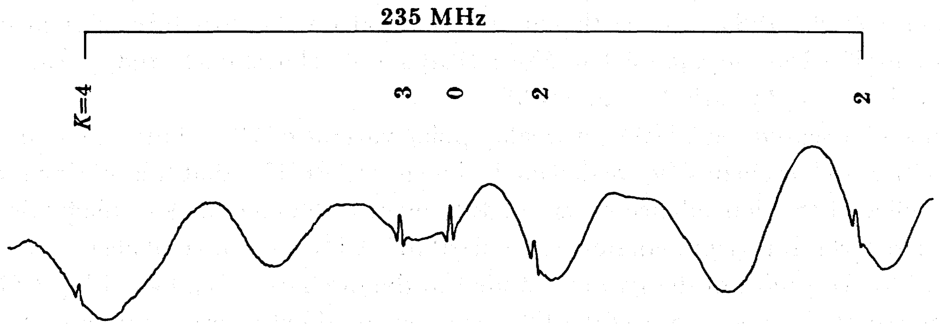

FIGURE 6. Overview of the DON_2^+ spectrum around 275 GHz showing the different K components of the $J = 13 \leftarrow 12$ transition. The carcinotron is used in the free-running mode.

TABLE 4. SPECTROSCOPIC CONSTANTS FOR THE GROUND STATE OF HCO_2^+ AND DCO_2^+ FROM EXTENDED WATSON'S S-REDUCED HAMILTONIAN IN THE I_r AXIS REPRESENTATION

A/MHz	788629 (3070)[a]	433038 (178)
B/MHz	10733.7221 (89)	10163.9589 (91)
C/MHz	10609.4435 (87)	9908.6414 (92)
D_J/kHz	3.5029 (33)	3.0999 (36)
D_{JK}/kHz	935.0 (18)	319.87 (12)
d_1/kHz	−0.0426 (70)	−0.1294 (63)
d_2/kHz	−0.0145 (22)	−0.0738 (67)
H_{KJ}/Hz	3786. (314)	−364.4 (40)
h_2/Hz	0[b]	0.057 (12)
L_{KJ}/Hz	79. (19)	0[b]
S_{KJ}/Hz	1.79 (38)	0[b]
κ	−0.9996	−0.9988

[a] Numbers in parentheses denote one standard deviation in the last digits.
[b] These constants were poorly determined and were therefore set equal to zero.

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† 1 kcal = 4.184×10^3 J.

A total number of 63 rotational lines for HON_2^+ and 89 for DON_2^+ characterized respectively by $5 \leqslant J \leqslant 18$, $K_a \leqslant 4$ and $0 \leqslant J \leqslant 17$, $K_a \leqslant 7$, were measured in the 130–405 GHz frequency range. They have been fitted by using Watson's S-reduced hamiltonian, and the spectra of both HON_2^+ and DON_2^+ are reproduced within 23 kHz. Because both a-type and b-type transitions have been measured, an accurate set of molecular parameters has been determined. This set is as complete as is available for the isoelectronic stable molecule HNCO (Hocking *et al.* 1975). The results will be published elsewhere.

Finally, note that an extensive search for the N-protonated form has been unsuccessful.

4.4. *A weakly bound ionic cluster:* $Ar \cdot H_3^+$

Gas-phase ionic clusters are present in a number of physical-chemical systems, such as in flames or in the upper atmosphere, and are generally though to play an important role in situation where ions are involved and where stabilization of the complex can occur via collisions or radiative transitions (Castleman & Keesee 1986). Although there is a growing interest in the study of the dynamics of their formation and photodissociation, very little is known about the spectroscopic properties of these species. In addition to the pioneering work of Schwarz (1977), only a few low-resolution spectra have been obtained: in the visible, for clusters like $Ar \cdot C_6F_6^+$ by Dimauro *et al.* (1984) and in the infrared, for clusters like H_{2n+1}^+ or $H_3O^+(H_2O)_n$ by Okumura *et al.* (1985). In particular, information on the structure of such complexes comes essentially from *ab initio* calculations (Raynor & Herschbach 1983; Ahlrichs 1975; Yamagucchi *et al.* 1983; Frisch *et al.* 1986).

In course of a search for CH_2D^+, a weakly polar variant of CH_3^+ that is thought to play a key role in interstellar chemistry, we detected a line near 390 GHz that was ascribed to an ionic species in view of the dependence of its intensity against the confinement magnetic field (see figure 4). However, it was immediately recognized that CH_4 was not at all necessary to produce this ion. Moreover, most of the gases we added to the discharge (N_2, O_2, C_2H_2, CO, Kr) led to the immediate disappearance of the line, even when added in trace amounts. In contrast, addition of H_2 and of compounds with a proton affinity lower than that of hydrogen (Ne, He) led only to a slight decrease of the line intensity. Clearly the ion was formed with only Ar and/or D atoms. By scanning ±2.5 GHz around the line frequency we discovered only four additional lines. This set of five lines showed the characteristic K pattern expected for a $J \geqslant 2$ a-type ^qR rotational transition of a slightly asymmetric prolate rotor. By carefully exploring a frequency range of about 40 GHz with the free running carcinotron, we found another characteristic set of five lines. A fit of these 10 lines with Watson's A-reduced hamiltonian led to the determination of the molecular constants A, B, C and of four centrifugal distortion parameters. The value of the inertial defect ($\Delta = 0.11$ u Å^2†) clearly indicated that the molecule was planar and the relative intensities of the K components were consistent with a C_{2v} symmetry. Comparison of the A value (655137 MHz) with that of D_3^+ (654266 MHz) strongly suggested that a D_3^+ ion was involved in the molecule; this was also supported by the similar intensity behaviour of the H_2D^+ line and of the unknown lines against the confinement magnetic field (figure 4). The relatively low values of B and C, however, suggested that one heavy atom was involved in the molecule, most probably Ar in view of previously mentioned chemical evidence.

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† $1\ \text{Å} = 10^{-10}\ \text{m} = 10^{-1}\ \text{nm}$.

By analogy with the $He \cdot H_3^+$ and $H_2 \cdot H_3^+$ clusters, well characterized by *ab initio* calculations (Poshusta & Agrawal 1973; Ahlrichs 1975; Raynor & Herschbach 1983; Dykstra 1983; Yamaguchi *et al.* 1983), we assumed that the Ar atom lay on a symmetry axis of the D_3^+ triangle, which we assumed to be little disturbed by the presence of Ar. By adjusting the distance between Ar and D_3^+, we were able to account for the molecular constants within 3×10^{-3} and to predict the $Ar \cdot H_3^+$ spectrum, which was sought by just replacing D_2 by H_2. The $Ar \cdot H_3^+$ lines were found very close to the predicted frequencies (within less than 2×10^{-3}), thus confirming the identification of the ion and of its structure (Bogey *et al.* 1987).

$Ar \cdot H_3^+$ appears to be planar with the Ar lying on a symmetry axis of H_3^+ at 2.38 Å from the H_3^+ centroid. From such a structure, a very large dipole moment is expected (of the order of 9 D) and explains why we detected this complex in spite of experimental conditions *a priori* not favourable to cluster production.

Study of the mixed isotopic forms $Ar \cdot H_2D^+$ and $Ar \cdot HD_2^+$ is now in progress and some lines have already been observed at frequencies in complete agreement with those predicted with the structure given above. A number of the lines observed for the four isotopic forms are in fact doublets (figure 7), showing that tunnelling motions occur. When quantitatively interpreted, these results will lead to the determination of an accurate substitution structure and will shed light on the dynamics of such ionic clusters, a first step towards the study of other complexes such as $H_2 \cdot H_3^+$.

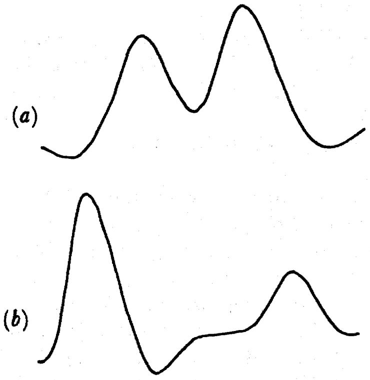

FIGURE 7. Two examples of tunnelling motion doublets observed in the $Ar \cdot H_3^+$ complex. (*a*) The $12_{0,12} \leftarrow 11_{0,11}$ transition of $Ar \cdot D_3^+$ near 390.3 GHz. The splitting is 800 kHz. (*b*) The $9_{0,9} \leftarrow 8_{0,8}$ transition of $Ar \cdot HDH^+$ near 399.4 GHz. The splitting is 5.5 MHz.

5. CONCLUSION

Major improvements in ion-production methods as well as in spectrometer sensitivity and frequency coverage have made possible the recent impressive developments in the field of ion high-resolution rotational spectroscopy. In particular, the close coupling between radioastronomy and laboratory spectroscopy, which have been intimately linked since the detection of the first ion, have led in the last three years to the interstellar detection of fundamental species such as H_2D^+ (Phillips *et al.* 1985), $HCNH^+$ (Ziurys *et al.* 1986) and H_3O^+ (Hollis *et al.* 1986; Wootten *et al.* 1986), thus giving new insights into interstellar chemistry. Spectroscopic studies of molecular ions can now be as complete as those of stable molecules, and molecular structures of ions have been derived (Woods *et al.* 1981; Bogey *et al.* 1981; Szanto *et al.* 1981; Gudeman

& Woods 1982; Bogey *et al.* 1986*a*). Further developments can now be expected from the interactions between the very active fields of radioastronomy, *ab initio* calculations, infrared (IR) and millimetre-wave spectroscopy. The detection of new objects, which was anticipated for a few years (Woods 1983; Gudeman & Saykally 1984) is now a reality, because negative ions, which have already been detected in IR (Owrutsky *et al.* 1985; Liu & Oka 1986; Tack *et al.* 1986; Kawaguchi & Hirota 1986; Brown *et al.* 1986; Gruebele *et al.* 1987) will, without doubt, be observed in the millimetre-wave range in the near future. The recent detection of the $Ar \cdot H_3^+$ ionic cluster in a plasma is a stimulating challenge for both experimentalists and theoreticians to detect other similar species.

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Discussion

E. HIROTA (*Institute for Molecular Science, Okazaki* 444, *Japan*). Professor Destombes has explained the doublet structure observed for some lines of $\mathrm{Ar \cdot D_3^+}$ in terms of the internal rotation of the D_3 group. Then he should observe the effect of the spin statistics on the doublets. Did he really observe such statistical weights?

J. L. DESTOMBES. The CNPI group of $\mathrm{Ar \cdot D_3^+}$ is G_{12} and it can be used to predict the statistical weights of the energy levels. The observed line intensity ratios of the doublets are in good agreement with these predictions (see table IV in Bogey *et al.* 1987). The same agreement has been found for the other isotopic forms.