

## MICROWAVE SPECTROSCOPY OF MOLECULAR IONS IN THE LABORATORY AND IN INTERSTELLAR SPACE

R. Claude Woods  
University of Wisconsin--Madison  
Department of Chemistry  
1101 University Avenue  
Madison, Wisconsin 53706  
USA

**ABSTRACT.** Refinements of the instrumentation and methods used for laboratory microwave spectroscopy of molecular ions in the last few years have led to successful observation of spectra of several new molecular ions of particular astrophysical interest. Notable among these enhancements have been the use of magnetic fields to increase the density of ions in discharge plasmas and the extension of upper frequency limits of the spectrometers towards and into the sub-millimeter regime. The number of ions now observed by laboratory microwave spectroscopy is more than a dozen, and about two thirds of these have also been detected, at least tentatively, by radioastronomy. Even where detections are uncertain or impossible, useful upper bounds on ion abundances can be gleaned from radioastronomical observations once exact transition frequencies and assignments are known from laboratory studies. Special attention will be given in this presentation to the status of laboratory and radioastronomical work on  $\text{HOC}^+$ ,  $\text{H}_2\text{D}^+$ , and  $\text{SO}^+$ , molecular ions which have been the object of our own recent interest and effort in this area.

### 1. INTRODUCTION

Progress in radioastronomy has always depended heavily upon a base of data obtained from laboratory microwave spectroscopy. For most stable molecules with any reasonable likelihood of being observable interstellar species, laboratory measurements of frequencies and assignments of transitions in any frequency range of interest are straightforward with currently available equipment. Observation of laboratory spectra of transient species, on the other hand, remain a great challenge to the experimentalist. Since so many of the species likely to be detected by radioastronomy in the future are transient ones and since transient species often provide particularly helpful clues to understanding the overall reaction mechanisms in the interstellar environment, advances in laboratory spectroscopic technique are important to the continued healthy development of the field of astrochemistry. The present discussion will focus in particular on

studies of molecular ions, although the microwave spectroscopic study of neutral free radicals or other unstable molecules has shown a parallel rapid development in recent years, often utilizing rather similar experimental techniques.<sup>1</sup> Even within the limits of molecular ion studies this paper is in no way intended to be a comprehensive review or claimed to be a perfectly evenhanded treatment of all the work in the field. Some developments of technique that the author feels are particularly significant will be described briefly, and then recent studies of individual molecular ions of astrochemical interest will be discussed, with some emphasis on those with which the author has had some personal involvement.

## 2. DEVELOPMENTS IN TECHNIQUE

One major trend of the past several years has been the extension of the available frequency range in many laboratories. Accessibility of frequencies up to 400 or 500 GHz is now available to most of the microwave spectrometers that are being used for work on molecular ions, while all work up until about 1981 had been restricted to frequencies below 125 GHz. In most cases high frequency radiation is generated in harmonic generator diodes pumped by lower frequency klystrons, and detection is done with InSb photoconductive crystals at liquid helium temperature. In some instances a fundamental oscillator, a BWO (Carcinotron), has been available at submillimeter wave frequency, giving much greater power and consequently much greater sensitivity than the harmonic generation scheme. Such a Carcinotron source has been used at Lille University by Destombes and coworkers to great advantage in several recent new observations (*vide infra*). Generally the increased frequency diversity is very helpful (1) because transition intensities increase very rapidly with frequency, (2) plasma noise, attenuation, etc., go down rapidly with frequency, (3) observation of transitions at several  $J$  values greatly increases spectral information content and facilitates assignment of new spectra, and (4) light hydride molecules with no lines at all at lower frequencies become observable in the submillimeter range. Some evolutionary progress has also been achieved in phase-lock methods, computer control schemes, etc., and these have gradually improved spectrometer sensitivity. A different route to improvement comes through increasing the efficiency of the production of molecular ions for study. Probably the greatest advance in this area has been the application of axial magnetic fields to glow discharges. This method was invented and developed by De Lucia and coworkers at Duke University, who observed increases of absorption intensities of factors of 20 to 100, depending on geometry and other variables, when fields of about 300 G were applied.<sup>2</sup> They have explained the effect as an extension of the length of the negative glow region of the discharge.<sup>2</sup> Numerous other types of plasma or discharge production have been or are being tried in various laboratories. Another development that certainly has had a major impact on the detection of new

microwave spectra of molecular ions is the new availability of high resolution laser infrared spectra for such species. In several important cases prior analysis of infrared data greatly narrowed the microwave search range and contributed heavily to the detection of molecular ion spectra in the microwave region. Historically ab initio quantum chemical calculations have played an important role in the location and identification of new molecular ion spectra, and as their accuracy has been steadily improved such theoretical calculations have become increasingly valuable to spectroscopists working in this area. We will now further illustrate some of these points by a consideration of some specific molecular ions.

### 3. INDIVIDUAL MOLECULAR IONS

#### 3.1 HOC<sup>+</sup>

In 1981-82 we were finally able to detect the laboratory spectrum ( $J = 0-1$  transition) of the normal,  $^{13}\text{C}$ , and  $^{18}\text{O}$  forms of HOC<sup>+</sup>, the isoformyl ion.<sup>3</sup> The availability of the transition frequency then made possible a radioastronomical search for HOC<sup>+</sup>, which covered many sources. In all of them it could be demonstrated that the HOC<sup>+</sup> abundance was at least two orders of magnitude less than that of the familiar HCO<sup>+</sup> isomer, which yields strong emission in all the sources.<sup>4</sup> In only one source, Sgr B2, was a line observed at the correct frequency. This was tentatively assigned to HOC<sup>+</sup>, with the normal reservations pertaining to a detection of a single line in a single source, and the low emission intensity corresponded to a HCO<sup>+</sup>/HOC<sup>+</sup> abundance ratio of 330 if the assignment was accepted. The correctness of this assignment and the actual value of the abundance ratio in typical interstellar clouds have since become very controversial matters, but at the very least it may be claimed that the interest in these issues has stimulated a great deal of further theoretical and experimental work on the chemistry of HOC<sup>+</sup>, which was largely uncharted in 1982. The relative rates of formation of the two isomers in proton transfer to CO from H<sub>3</sub><sup>+</sup>, and the loss rates of the HOC<sup>+</sup> by reaction with H, CO, H<sub>2</sub> and other species have all been discussed and studied, and the ideas about these rates have changed several times since Reference 4, which proposes a simple model for explaining the abundance ratio, was written. Notably, a recent paper by Wagner-Redeker, et al.<sup>5</sup> has claimed that HOC<sup>+</sup> is rapidly destroyed by reaction which H<sub>2</sub>, even at interstellar temperatures, and another recent paper by McMahon and Kebarle<sup>6</sup> has claimed that HOC<sup>+</sup> can indeed be efficiently formed by proton transfer from H<sub>3</sub><sup>+</sup> to CO. Many further pertinent references to HOC<sup>+</sup> chemistry and much discussion can be found in those two articles. Spectroscopic work has continued on HOC<sup>+</sup> in various laboratories. Soon after the astronomical search the higher J lines of the normal species were detected at Duke,<sup>7</sup> and recently the DOC<sup>+</sup> spectrum has been assigned at Lille.<sup>8</sup> We have recently seen high J lines for HO<sup>13</sup>C<sup>+</sup> and detected H<sup>18</sup>O<sup>13</sup>C<sup>+</sup>.<sup>9</sup> All these later works involved magnetic field

enhancement of the ion density, and by now leave absolutely no doubt as to the assignment of the laboratory spectrum of  $\text{HOC}^+$

### 3.2 $\text{H}_2\text{D}^+$

In June, 1984 we were able to detect the  $1_{10}-1_{11}$  transition of  $\text{H}_2\text{D}^+$  in a magnetically confined glow discharge in Ar- $\text{H}_2$ - $\text{D}_2$  mixtures.<sup>10</sup> At the same time Bogey et al.<sup>11</sup> also detected the same line in very similar discharge conditions. The work at Lille used the Carcinotron source while that at Wisconsin relied on harmonic generation techniques. Both studies were greatly facilitated by the availability of the infrared data and analysis on  $\text{H}_2\text{D}^+$  by Amano and Watson.<sup>12</sup> Using the laboratory frequency an astronomical search<sup>13</sup> for  $\text{H}_2\text{D}^+$  was made in January, 1985 using the Kuiper Airborne Observatory operated by NASA. This was required because atmospheric water vapor attenuation is severe at 372 GHz, where this  $\text{H}_2\text{D}^+$  transition occurs. We did observe a line at the correct frequency in NGC 2264, a giant molecular cloud, and failed to do so with similar integration time in TMC1, a cool dark cloud.<sup>13</sup> This can be interpreted as supporting at least a partial equilibration of ortho and para hydrogen in these interstellar sources. If the o/p ratio were statistical, then one would expect emission in TMC1, where  $\text{H}_2\text{D}^+$  is expected to be very abundant, to be quite strong. If the assignment of the observed emission in NGC 2264 to  $\text{H}_2\text{D}^+$  is the correct one, then this would represent the first actual observation of any isotopic variant of  $\text{H}_3^+$  in the interstellar medium. The observed emission intensity corresponds to  $n(\text{H}_3^+)/n(\text{H}_2)$  in the range  $7 \times 10^{-10}$  to  $2 \times 10^{-9}$  in NGC 2264, and these values are reasonably consistent with the predictions of current models of the ion molecule chemistry.<sup>14-16</sup>

### 3.3 $\text{HOCO}^+$

In 1981 Thaddeus et al.<sup>17</sup> found the spectrum of a near-linear molecule in Sgr B2 and proposed that it was either due to  $\text{HOCN}$  or  $\text{HOCO}^+$ . Recent laboratory work by Bogey et al.<sup>18</sup> has shown conclusively that the carrier of that spectrum was indeed the ion  $\text{HOCO}^+$ . Using the Carcinotron source in the range 340-370 GHz and a magnetically confined glow discharge they detected and assigned several transitions that were entirely consistent with the earlier astronomical frequencies of several lower J lines.<sup>17</sup> Thus  $\text{HOCO}^+$  can now be considered to be firmly established as an observed interstellar species.

### 3.4 $\text{HCNH}^+$ and $\text{H}_3\text{O}^+$

These two astrophysically important ions have been recently observed at millimeter and sub-millimeter wavelengths in magnetically confined glow discharges, and in both cases earlier analysis of the high resolution infrared spectrum was critical to the location and assignment of the microwave spectrum. The  $\text{H}_3\text{O}^+$  ion has an inversion type band for

which a few of the P branch type transitions occur in the vicinity of 300 GHz. Plummer et al.<sup>19</sup> observed the  $J = 2$  line (307 GHz) and Bogey et al.<sup>20</sup> have observed the  $J = 3$  lines (365, 388, and 396 GHz). Both were guided by the infrared study of Liu and Oka.<sup>21</sup> Several rotational transitions of  $\text{HCNH}^+$  were recently detected by Bogey et al.<sup>22</sup> That microwave search relied on the infrared analyses of Amano<sup>23</sup> and of Altman, et al.<sup>24</sup>

### 3.5 $\text{SO}^+$

We were able in early 1985 to detect several transitions in the laboratory microwave spectrum of the  $\text{SO}^+$  molecular ion.<sup>25</sup> The search was guided by the molecular constants from the recent optical work of Hardwick et al.<sup>26</sup> The magnetic field did not appear to greatly enhance the signal strength in this case, but the magnet availability still proved very helpful in distinguishing (via the Zeeman effect) the  $\text{SO}^+$  lines from the profusion of lines of other species. The ground state is  $^2\Pi_{1/2}$ , and it exhibits a very characteristic, very slow Zeeman effect. We were able to assign 5 transitions by the Zeeman effect and determine  $B_0$ ,  $D_0$ , and  $P_0$  (the lambda doubling parameter). In September, 1985 an astronomical search for the  $J = 3/2 - 5/2$  doublet of  $\text{SO}^+$  at 15.8 GHz and 16.2 GHz was carried out by Churchwell and Woods<sup>27</sup> at NRAO, Kitt Peak. We believe that we detected both lines in ORION A and DR21-OH and one of them in NGC 2264. Further work aimed at confirming and extending these observation is planned. Ultimately data on  $\text{SO}^+$  promises to be very helpful in furthering the understanding of the sulfur chemistry of the interstellar medium. The initial indication seems to be that  $\text{SO}^+$  may yield detectable, though weak, emission in a variety of astrophysical sources.

### 3.6 Other Molecular Ions

The list of molecular ions observed by microwave spectroscopy in the laboratory now includes 14 ions. In addition to those discussed above are  $\text{HCO}^+$ ,<sup>28</sup>  $\text{HN}_2^+$ ,<sup>29</sup> and  $\text{HCS}^+$ ,<sup>30</sup> that are already very well established as interstellar species, and  $\text{CO}^+$ ,<sup>31</sup>  $\text{NO}^+$ ,<sup>32</sup>  $\text{ArD}^+$ ,<sup>33</sup> and  $\text{KrD}^+$ ,<sup>34</sup> which are not expected to be detectable in the interstellar medium. The diatomic species  $\text{OH}^+$  has been detected<sup>35</sup> by far infrared laser side band spectroscopy, which is very similar to microwave spectroscopy, but somewhat out of the usual microwave frequency range. This list of ions studied can be expected to expand rapidly in the future, and several of the new species will likely be of considerable astrochemical interest.

## 4. REFERENCES

1. E. Hirota, High-Resolution Spectroscopy of Transient Molecules, Springer-Verlag, Berlin, 1985.

2. F.C. DeLucia, E. Herbst, G.M. Plummer, and G. Blake, *J. Chem. Phys.* **78**, 2312 (1983).
3. C.S. Gudeman and R.C. Woods, *Phys. Rev. Lett.* **48**, 1344 (1982).
4. R.C. Woods, C.S. Gudeman, R.L. Dickman, P.F. Goldsmith, G.R. Huguenin, W.M. Irvine, A<sup>0</sup>. Hjalmarson, L.-Å. Nyman, and H. Olofsson, *Astrophys. J.* **270**, 583 (1983).
5. W. Wagner-Redeker, P.R. Kemper, M.F. Jarrold, and M.T. Bowers, *J. Chem. Phys.* **83**, 1121 (1985).
6. T.B. McMahon and P. Kebarle, *J. Chem. Phys.* **83**, 3919 (1985).
7. G.A. Blake, P. Helminger, E. Herbst and F.C. DeLucia, *Astrophys. J.* **264**, L69 (1983).
8. M. Bogey, C. Demuyneck, and J.L. Destombes, to be published.
9. H.E. Warner and R.C. Woods, to be published.
10. H.E. Warner, W.T. Conner, R.H. Petrmichl, and R.C. Woods, *J. Chem. Phys.* **81**, 2514 (1984).
11. M. Bogey, C. Demuyneck, C. Denis, J.L. Destombes, and B. Lemoine, *Astr. Ap.* **137**, L15 (1984).
12. T. Amano and J.K.G. Watson, *J. Chem. Phys.* **81** 2869 (1984).
13. T.G. Phillips, G.A. Blake, J. Keene, R.C. Woods, and E. Churchwell, *Astrophys. J.* **294**, L45 (1985).
14. S.S. Prasad and W.T. Huntress, Jr., *Ap. J. Suppl.* **43**, 1 (1980).
15. T.E. Graedel, W.D. Langer, and M.A. Frerking, *Ap. J. Suppl.* **48**, 321 (1982).
16. C.M. Leung, E. Herbst, and W.F. Heubner, *Ap. J. Suppl.* **56**, 231 (1984).
17. P. Thaddeus, M. Guelin, and R.A. Linke, *Astrophys. J.* **246**, L41 (1981).
18. M. Bogey, C. Demuyneck, and J.L. Destombes, *Astr. Ap.* **138**, L11 (1984).
19. G.M. Plummer, E. Herbst, and F.C. DeLucia, *J. Chem. Phys.* **83**, 1428 (1985).

20. M. Bogey, C. Demuynck, M. Denis, and J.L. Destombes, *Astr. Ap.* July, 1985.
21. D.J. Liu and T. Oka, *Phys. Rev. Lett.* **54**, 1786 (1985).
22. M. Bogey, C. Demuynck, and J.L. Destombes, *J. Chem. Phys.* **83**, 3703 (1985).
23. T. Amano, *J. Chem. Phys.* **81**, 3350 (1984).
24. R.S. Altman, M.W. Crofton, and T. Oka, *J. Chem. Phys.* **81**, 4255 (1984).
25. N. Carballo, H.E. Warner and R.C. Woods, to be published.
26. J.L. Hardwick, Y. Luo, D.H. Winicur, and J.A. Coxon, *Can. J. Phys.* **62**, 1792 (1984).
27. E. Churchwell and R.C. Woods, to be published.
28. R.C. Woods, T.A. Dixon, R.J. Saykally, and P.G. Szanto, *Phys. Rev. Lett.* **35**, 1269 (1975).
29. R.J. Saykally, T.A. Dixon, T.E. Anderson, P.G. Szanto and R.C. Woods, *Astrophys. J.* **205**, L101 (1976).
30. C.S. Gudeman, N.N. Haese, N.D. Piltch, and R.C. Woods, *Astrophys. J.* **246**, L47 (1981).
31. T.A. Dixon and R.C. Woods, *Phys. Rev. Lett.* **34**, 61 (1975).
32. W.C. Bowman, E. Herbst, and F.C. DeLucia, *J. Chem. Phys.* **77**, 4261 (1982).
33. W.C. Bowman, G.M. Plummer, E. Herbst, and F.C. DeLucia, *J. Chem. Phys.* **79**, 2093 (1983).
34. H.E. Warner, W.T. conner, and R.C. Woods, *J. Chem. Phys.* **81**, 5413 (1984).
35. J.P. Bekooy, P. Verhoeve, W.L. Meerts, and A. Dymanus, *J. Chem. Phys.* **82**, 3868 (1985).

## DISCUSSION

D'CUNHA: We have recently started some studies on molecular ions. I was interested in your line broadening studies on the  $\text{HCO}^+$  ion. Do you take into account the Stark broadening also when you are talking about pressure broadening?

WOOD: We have been working on Stark broadening and for that particular line it will be quite negligible. We are quite sure of it. We have looked at the vibrationally excited lines, the L doublet lines. We are doing some collaborative work with Garbelle of University of Bologna in Italy. Basically if you go to these degenerate states, the effect becomes much faster. Then you have a chance to see it and we have also been working on the HCN in the excited state in the same plasmas and trying to look at the Stark effect  $2^2$  vibrations of state which is very closely degenerate. And sure enough, we have observation of Stark effect. This will be very small in the case of ground vibrational state such that it will never compare with the pressure broadening.

D'CUNHA: In the study of isotopic molecules in the discharge tubes, do you use flowing system?

WOOD: Yes. It is a flowing system but the pressure is very low. The partial pressures of the reactive gases are very small so that one can afford to have flowing gases.

M. SINGH: You recall, you have mentioned in the beginning of the talk that you record the microwave spectra of HNC and HCN. In getting the spectra of these two radicals, you used different parent compounds or you have a different way of producing these radicals? We have observed in our laboratory the visible or UV spectra of HNC. As you have observed in microwave, I would like to know whether you have used the same parent compound or the method you have used is different.

WOOD: The production is exactly the same as that for the ions - the same plasma field, the same DC discharge, no magnetic field. The chemistry is really variable. One can use many combinations of gases: HNC and HCN are both formed almost in any combination with right elements. The best combination is Argon mixed with nitrogen and some methane, and both these species are present at the same time along with other radicals.

VENUGOPAL: I would like to know your  $\text{SO}^+$  observations. What is the integration time that has been used?

WOOD: Typically 4 hours scan. Essentially complete night was used for each source, although the Orion spectrum that showed both the plateau and the ridge feature actually was accumulation of observations of three different nights with a total of about 12-15 hr of observing time.

EVERY: What is the problem with confirming  $\text{HCO}^+$ ? Presumably you looked for the next higher harmonic. Why haven't you seen it or have you seen it?



WOOD: We have not yet looked for it. It is not clear it will resolve the problem because of the excitation. The latest modelling seems to show that  $\text{HCO}^+$  will be seen if it is in a low pressure region. In such a region it may not be excited and so it is difficult to see. It is worth trying out.

GUELLIN: I have a new candidate for your  $\text{HCO}^+$  line. It is SIS 33.

P.K. GHOSH: (i) Do you do any diagnostic of the plasma? (ii) What is the absolute concentration of  $\text{N}_2\text{H}^+$  in the experiment that you have done and (iii) What is the enhancement that you get at 300 gauss?

WOOD: Yes. We do diagnostics. Several plans in which we try to look at the relative intensities of the vibrational lines to measure vibrational temperature and rotational temperatures from rotational line intensities. One can look at the widths in high pressure range to get the line broadening, at low pressure range or high frequency range the Doppler broadening is dominant to get the transitional temperatures of the ions. The Stark broadening that we have just mentioned is another diagnosis to determine the electric field in the discharge. (ii) The ion density is about  $10^{-5}$  to the overall gas density i.e.  $10^{10}$  ions  $\text{cm}^{-3}$  or a little more. (iii) In the magnetic field, the enhancement observed is between 20 to 100.

P.A. FELDMAN: Is it absolutely ruled out that at the present time with the current spectroscopic information that in spite of its high excitation, the  $J=3$  line of  $\text{H}_2\text{D}^+$  cannot be the unidentified 45379 line?

WOOD: I cannot say as it has not been observed in the laboratory. It is unlikely but not absolutely ruled out.

TURNER: Is it not the case that the Nobiyama line has been seen only in TMC-1 which is a cold cloud. Therefore, the energy that you state will be totally impossible for this species.

OMONT: (i) What is the chance that one can have the frequency of  $\text{C}_2\text{H}_3^+$  in not far future and (ii) of the neutral radicals that you mentioned.

WOOD: (i) The structure is non-classical and because of much tunnelling it will be very complicated spectroscopically. (ii) Much progress is going on in the field of neutral radicals and the situation changes from day to day and from week to week. Hence anything is possible.

IYENGAR: What was the line flux that was obtained in NGC 2264 with line 75  $\text{H}_2\text{D}^+$  and what was the type of detector used?

WOOD: The detector used is Tom Phillips detector which has been used for several detections including HCl. It is Indium-antimonide crystal in liquid helium. It is a heterodyne system with a very large band width. The intensity of the  $\text{H}_2\text{D}^+$  line is a few tenths of °K.