

Infrared Spectroscopy of Molecular Ions

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Following is a brief summary of infrared spectroscopy of molecular ions since June 1984 when I gave a talk at the Columbus Meeting. I limit myself to works done in our laboratory and other works closely related to them.

1. H_3^+

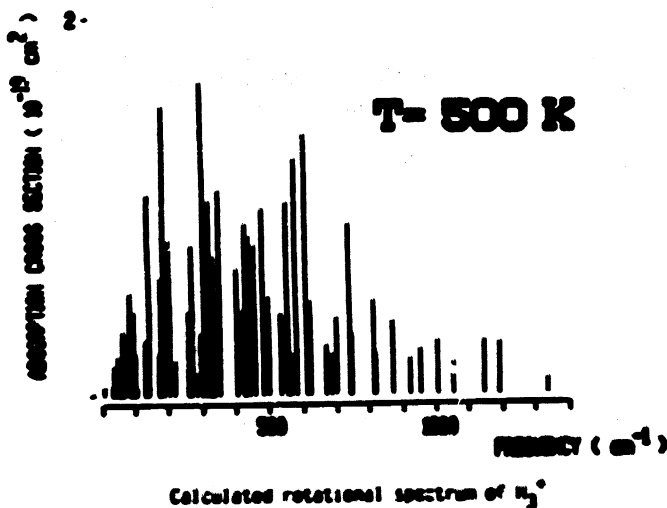
A detailed analysis of the ν_2 vibration-rotation band has been completed by Watson et al.¹ in which the originally reported 15 lines² and the subsequently reported 15 lines³ were added with another 16 lines of higher rotational levels and lower frequency P branch transitions to determine accurate molecular constants of this fundamental ion. Because of the large vibration-rotation constants of H_3^+ , the Pade approximation has proved useful. The determined constants are shown on the following page.

Amano and Watson^{4,5} observed and analyzed the ν_1 fundamental band of H_2D^+ which enabled them to accurately predict the H_2D^+ rotational lines in the millimeter wave region. Following their predictions, the rotational transitions $1_{1,0} - 1_{1,1}$ ^{6,7} and $2_{1,1} - 2_{1,2}$ ⁸ have been detected. Based on this laboratory data a possible detection of the $1_{1,0} - 1_{1,1}$ transition of H_2D^+ in the giant molecular cloud NGC 2264 has been reported⁹. The ν_2 and ν_3 band of H_2D^+ which was initially reported by Shy et al.¹⁰ without assignment has been studied more extensively and analyzed¹¹. Because of the large molecular constants and the Coriolis coupling between the two states, supermatrix approach was used to eliminate ambiguity in assignment. Doubly deuterated species HD_2^+ has been studied (ν_1 band¹², and ν_2 and ν_3 band¹³). Rotational spectrum of this species should also be observable in the millimeter wave region.

Vibration-rotation parameters for the ν_1 band of H_3^+ (cm^{-1})

Parameter	Value (SD) ¹	Correlation $\alpha.3$	Ab. meter ²	Ab. meter ³
Ground state				
B_0	43 564570(1553)	163.2	43 658	43 520
C_0	20 605147(7993)	167.7	20 675	20 579
$10^2 D_0''$	4.17537(1900)	2 248.5	3.72	4.22
$10^2 D_0^{a,a}$	-7.60636(4096)	3 332.9	-6.70	-7.76
$10^2 D_0^{a,b}$	3.74107(3683)	1 797.7	3.29	3.85
$10^2 A_0$	-1.056(100)	5.7		-0.9
$10^2 d_0$	1.7325(1529)	346.6		2.0
$10^2 e_0$	-4.1003(4478)	190.4		-4.6
ν_1 state				
ν_1	2521 408(7925)	18.2	2516	2494.4
B_1	44.225698(3011)	242.1	43 839	
C_1	19.339581(6389)	1 000.8	19 735	
C_2	-18.65110(384)	49.7	-18.516	
$10^2 \eta_1^2$	-14.0319(858)	691.4		
$10^2 \eta_2^2$	16.7714(1937)	2 659.1		
$10^2 D_1''$	5.27821(3051)	7 814.5		
$10^2 D_1^{a,a}$	-10.87796(9077)	36 917.6		
$10^2 D_1^{a,b}$	6.07921(6385)	12 807.9		
$10^2 \rho_1$	-3.1598(363)	3.3		
ρ_2	-5.37192(254)	33.8	-4.87	
$10^2 A_1$	-1.056(100)	5.7		
$10^2 d_1$	2.0467(1481)	691.2		
$10^2 e_1$	-1.8823(3657)	1010.0		
$10^2 e_2$	4.0396(307)	263.6		
$10^2 e_3$	-7.1747(1467)	1772.6		

An exciting development was the observation of strong H_3^+ emission spectrum by Majewski et al.¹⁴ using a Fourier Transform spectrometer. A calculation of distortion induced rotational transitions of H_3^+ has been completed¹⁵.



2. HCNH^+

Based on the molecular constants of HCNH^+ determined from the infrared spectrum¹⁶ of HCNH^+ , Bogey et al.¹⁷ have observed rotational spectrum of the ion in the millimeter wave region. The radio astronomical detection of this ion has not been successful yet. Amano has studied several isotopic species and hot bands of this ion and determined the molecular structure accurately^{18,19}

3. H_3O^+

A systematic diode laser spectroscopy of the ν_2 vibration-inversion bands of H_3O^+ has led to an accurate determination of the ground state inversion doubling of this important ion.

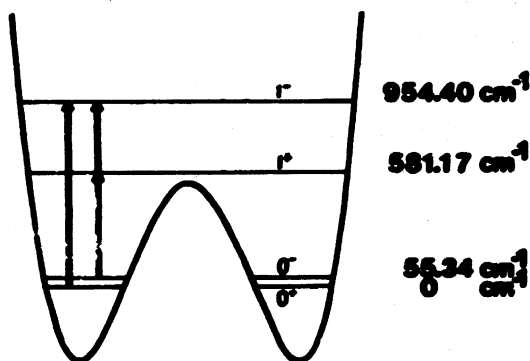


FIG. 1. The double minimum potential and the vibration-inversion energy levels of the ν_2 bending mode of H_3O^+ . The three infrared bands $1^- - 0^-$, $1^+ - 0^-$, and $1^- - 1^+$ shown by the bold arrows appear at 10.5, 19, and 27 μm , respectively. The ground-state inversion splitting has been determined from the measurement of the $1^- - 1^+$ band, reported in this paper, and our previous measurements of the other two bands (Ref. 4).

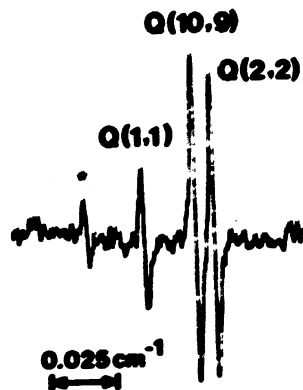


FIG. 2. The group of lines close to the origin of the $1^- - 1^+$ band. The derivative shape is due to velocity modulation (Ref. 14). The line with the asterisk is most likely the ground-state inversion-rotation transition $R(15, 9)$. Time constant of detection is 3 sec.

Following the initial study of the $1^- - 0^+$ transition in the 10μ region ($\nu_0 = 954.40 \text{ cm}^{-1}$)²⁰, the $1^+ - 0^-$ transition in 19μ ($\nu_0 = 525.83 \text{ cm}^{-1}$)²¹ and the $1^- - 1^+$ transition in 27μ ($\nu_0 = 373.23 \text{ cm}^{-1}$)²² have been observed and analyzed. This enabled us to calculate four submillimeter rotation-inversion lines of H_3O^+ . Based on this prediction the $0^- - 0^+$ P(2,1) transition²³ and the three $0^- - 0^+$ P(3,K) transition ($K = 2,1,0$)²⁴ have been measured. It is anticipated that these laboratory measurements will lead to radio astronomical detection of this ion which is predicted to be abundant in dense clouds.

The infrared spectroscopy of 10μ band was also reported by Lemoine and Destombes²⁵ and that of 19μ by Davies et al.²⁶ Sears has measured more R-brand lines of the $1^- - 1^+$ transition²⁷. Simultaneously analyzing these results, accurate molecular constants for the ν_2 vibration inversion levels have been determined²⁸. The prediction of millimeter wave and far infrared transitions related to metastable levels of H_3O^+ are listed below.

Predicted inversion and inversion-rotation spectrum of H_3O^+ related to the metastable rotational levels (in cm^{-1})

Transition	Predicted	Observed
R(3,3)	143.6080(77) ^a	---
R(3,0)	141.1638(66)	---
R(2,2)	121.8437(47)	---
R(1,1)	99.4255(34)	---
Q(3,3)	66.4912(63)	---
Q(2,2)	66.2791(39)	---
Q(1,1)	66.2312(31)	---
F(1,0)	32.8454(30)	---
F(2,1)	10.2408(24)	10.24082 ^c
F(3,2)	-12.1678(46) ^b	-12.16831 ^d
F(3,1)	-12.9678(47) ^b	-12.96757 ^d
F(3,0)	-13.2196(47) ^b	-13.21821 ^d

^aNumbers in the parenthesis are uncertainties of the prediction.

^bFor those transitions the O^+ level is above the O^- level.

^cExperimental observation by Plummer, Herbst and De Lucia.

^dExperimental observation by Bogry, Demuyck, Denis and Destombes.

The detection of far-infrared direct inversion transitions in H_3O^+ is an exciting possibility.

4. CH_3^+ and Hydrocarbon Cation

Our search for hydrocarbon cations revealed a very rich group of spectral lines in the area of $3250\text{ cm}^{-1} - 2950\text{ cm}^{-1}$. The most dense group of lines show spacings of $\sim 2\text{ cm}^{-1}$ and is likely due to protonated acetylene. The pattern is basically that of an asymmetric rotor but deviates from it in detail. This may be due to the interconversion between the two theoretical predicted structures, the classical (formaldehyde shape) and the non-classical (bridged) which are predicted to have very close energy^{29,30,31}.

The other group of lines were much widely spaced and this was obviously due to hydrocarbon cations containing one carbon atom. Initially protonated methane CH_3^+ was suspected to be the carrier of this spectrum but the analysis revealed that it is CH_3^+ . With hindsight, the abundance of CH_3^+ in the methane discharge is not surprising because it does not react with H_2 to form CH_4^+ .

About 150 lines were measured and assigned to the ν_3 fundamental band of CH_3^+ . The molecular constants of this ion are shown in the following table³².

Molecular constants of CH_3^+ (in cm^{-1})^a

$\nu_0 - (1-c) cC' = 3107.0527 (70)$	
$C' - C'c - B' = -5.2244 (10) \quad (C'-B') - (C''-B'') = 0.0630 (16)$	
$B' = 9.2691 (13)$	$B'' = 9.3600 (15)$
$D'_J = 6.57 (29) \times 10^{-4}$	$D''_J = 7.25 (34) \times 10^{-4}$
$D'_{JK} = 13.46 (85) \times 10^{-4}$	$D''_{JK} = 14.5 (11) \times 10^{-4}$
$D'_{K^2} = 5.36 (57) \times 10^{-4}$	$D''_{K^2} = 4.98 (73) \times 10^{-4}$
$\eta'_J = -7.3 (17) \times 10^{-4}$	
$q = 9.94 (99) \times 10^{-3}$	$r_0 = 1.09151 (9) \text{ \AA}$

^a the numbers in parentheses are one standard deviation.

More detailed analysis of the CH_3^+ spectrum and other hydrocarbon cations are in progress.

5. Plasma Diagnosis Using Infrared Spectroscopy.

Possibility of observing infrared absorption lines of molecular ions makes it possible to analyze plasma conditions in detail. Thus we should be able to study concentrations of various ions (and free radicals), their vibrational, rotational, and translational temperatures, the drift velocity of ions, concentration distributions of ions and so on. The advantage of this method is that it is in-situ and non-intrusive unlike traditional methods. We also have quantum mechanical information and a reasonable space resolution. Some such work will be discussed.

References.

1. J.K.G. Watson, S.C. Foster, A.R.W. McKellar, P. Bernath, T. Amano, F.S. Pan, M.W. Crofton, R.S. Altman and T. Oka, *Can. J. Phys.* 62, 1875 (1984).
2. T. Oka, *Phys. Rev. Lett.* 45, 531 (1980).
3. T. Oka, *Phil. Trans. Roy. Soc. London Ser. A.* 383, 543 (1981).
4. T. Amano and J.K.G. Watson, *J. Chem. Phys.* 81, 2869 (1984).
5. T. Amano, *J. Opt. Soc. Amer.* B2, 790 (1985).
6. M. Bogey, C. Demuyne, M. Denis, J.L. Destombes, and B. Lemoine, *Astron. Astrophys.* 137, L15 (1984).
7. H.E. Warner, W.T. Conner, R.H. Petrmichl and R.C. Woods, *J. Chem. Phys.* 81, 2514 (1984).
8. S. Saito, K. Kawaguchi and E. Hirota, *J. Chem. Phys.* 82, 45 (1985).
9. T.G. Phillip, G.A. Blake, J. Keene, R.C. Woods and E. Churchwell, *Ap. J. Lett.* 294, L45 (1985).
10. J.T. Shy, J.W. Farley and W.H. Wing, *Phys. Rev.* A24, 1146 (1981).
11. S.C. Foster, A.R.W. McKellar, J.R. Peterkin, J.K.G. Watson, F.S. Pan, M.W. Crofton, R.S. Altman and T. Oka, *J. Chem. Phys.*, submitted.
12. K.G. Lubic and T. Amano, *Can. J. Phys.* 62, 1886 (1984).
13. S.C. Foster, A.R.W. McKellar and J.K.G. Watson, *Symposium on Molecular Spectroscopy, Columbus, Ohio (1985)*.
14. W.A. Majewsky, J.K.G. Watson and J.W.C. Johns, *Symposium on Molecular Spectroscopy, Columbus, Ohio (1985)*.
15. F.S. Pan and T. Oka, to be published.
16. R.S. Altman, M.W. Crofton and T. Oka, *J. Chem. Phys.* 80, 3911, 81, 4255 (1984).
17. M. Bogey, C. Demuyne and J.L. Destombes, *J. Chem. Phys.*, in press.
18. T. Amano, *J. Chem. Phys.* 81, 3350 (1984).
19. T. Amano and k. Tanaka, *Symposium on Molecular Spectroscopy, Columbus, Ohio (1985)*.
20. N.H. Fiase and T. Oka, *J. Chem. Phys.* 80, 572 (1984).

21. D.J. Liu, M.N. Haese and T. Oka, J. Chem. Phys. 82, 5368 (1985).
22. D.J. Liu and T. Oka, Phys. Rev. Lett. 54, 1787 (1985).
23. G.M. Plummer, E. Herbst and F.C. De Lucia, J. Chem. Phys. 83, 1428 (1985).
24. M. Bogey, C. Demuyck, M. Denis and J.L. Destombes, Astron. Astrophys. (1985).
25. B. Lemoine and J.L. Destombes, Chem. Phys. Lett. 111, 284 (1984).
26. P.B. Davies, P.A. Hamilton and S.A. Johnson, J. Opt. Soc. Amer. B2, (1985) in press.
27. T. Sears, private communication.
28. D.J. Liu, T. Oka and T. Sears, to be published.
29. W.A. Lathan, W.J. Hehre and J.A. Pople, J. Am. Chem. Soc. 93, 808 (1971).
30. J. Weber, M. Yoshimira and A.D. McLean, J. Chem. Phys. 64, 4159 (1976).
31. G.P. Raine and H. Schaeffer III, J. Chem. Phys. 81, 4034 (1984).
32. M.W. Crofton, W.A. Kreiner, M.-F. Jagod, B.D. Rehfuss and T. Oka, J. Chem. Phys., in press.