Fourier Transform Emission Spectroscopy of NeH$^+$

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The Fourier transform emission spectrum of NeH$^+$ was observed. The (1, 0), (2, 1), and (3, 2) vibration–rotation bands of ^{20}NeH$^+$; the (1, 0) and (2, 1) bands of ^{20}NeD$^+$; and the (1, 0) band of ^{22}NeH$^+$ were recorded from a copper hollow-cathode discharge in neon and hydrogen. Molecular constants, including Born–Oppenheimer breakdown parameters, were extracted from the data. © 1985 Academic Press, Inc.

I. INTRODUCTION

In recent years the high-resolution vibration–rotation spectra of all protonated rare gases (except XeH$^+$) have been observed. The very first work was the detection of two lines [$P(12)$ and $P(13)$] of the fundamental (1, 0) band of HeH$^+$ by Tolliver *et al.* (*1*) using Doppler-tuned ion-beam spectroscopy with a CO laser. The detection of the Fourier transform emission spectrum of many ArH$^+$ bands was accomplished by Brault and Davis (*2*) in 1982. In the same year a difference frequency laser spectrometer allowed the observation of NeH$^+$ (*3*) and additional HeH$^+$ (*4*) lines of the fundamental bands. The Fourier transform emission technique gave Johns the spectrum of KrH$^+$ and ArD$^+$, and additional ArH$^+$ lines (*5*).

Haese *et al.* exploited the Doppler-shift of the vibration–rotation lines of ArH$^+$ produced by ion drift in a glow discharge to measure ion mobility (*6*). The University of Chicago group was thinking along similar lines as Gudeman *et al.* (*7*), who developed the Doppler-velocity modulation technique of ion detection. Crofton *et al.* (*8*) applied the ion modulation technique to the detection of ^{3}HeH$^+$, ^{3}HeD^1, and ^{4}HeD^1 fundamental bands, and the ^{4}HeH$^+$ (2, 1) band. Quasibound vibration–rotation levels of HeH$^+$ (and isotopic derivatives) were measured by CO$_2$ laser-induced predissociation of an ion beam (*9*). Finally, the $J = 1 \leftarrow 0$ transitions of ArD$^+$ (*10*) and KrD$^+$ (*11*) were observed by millimeter wave absorption.

Ab initio calculations played a very useful and important role in this considerable body of experimental work. Since HeH$^+$ has only two electrons, very accurate calculations, including corrections to the Born–Oppenheimer approximation, have been published (*12*). Very high quality calculations for NeH$^+$ (*13*), ArH$^+$ (*14*), KrH$^+$ (*13*), and XeH$^+$ (*15*) have also been made, most notably by Rosmus. These calculations

greatly reduce the search problem for laser-based techniques by providing estimated molecular constants. In addition, they are helpful in confirming the species assignment since only the ion beam techniques provide mass spectrometric information. Ion concentration estimates require knowledge of absorption coefficients (or Einstein A coefficients for emission work) which are currently best provided by *ab initio* calculations. Reasonably accurate dipole moments and dipole moment derivatives are easily computed while experimental measurements are discouragingly difficult.

Only the fundamental bands of $^{20}NeH^+$ and $^{22}NeH^+$ were found in the difference frequency laser experiments of Wong et al. (*3*). Johns (*5*) was unable to observe NeH^+ by Fourier transform emission spectroscopy. It was noted, however, by one of the authors (J.W.B.) that NeH^+ occurred as an impurity in a titanium hollow-cathode discharge in neon, suggesting that infrared Fourier transform techniques had the required sensitivity to detect NeH^+. Titanium is a well-known hydrogen absorber. Using a copper hollow cathode and a neon discharge with a small amount of added hydrogen we were able to find the (1, 0), (2, 1), and (3, 2) bands of $^{20}NeH^+$; the (1, 0) band of $^{22}NeH^+$; and the (1, 0) and (2, 1) bands of NeD^+.

Although the Fourier transform emission experiments lack the sensitivity of laser experiments (particularly if ion velocity or discharge modulation is employed), there are certain advantages. The obvious one is that the entire spectrum can be recorded quickly without a wavelength search. Another advantage, not unique to Fourier transform methods, is that emission work usually provides more bands than absorption so that the potential energy surface of NeH^+ can be more thoroughly characterized.

II. EXPERIMENTAL DETAILS

The experimental conditions for the observation of NeH^+ and NeD^+ were identical to those for CuH (*16*) since NeH^+ and CuH were found at the same time. Briefly, the spectra were produced in a copper hollow-cathode lamp at a current of 330 mA. The lamp was operated with 2 Torr of Ne gas and 30 mTorr of H_2. For the NeD^+ experiment the H_2 was replaced with D_2.

The spectra were recorded with the Fourier transform spectrometer associated with the McMath Solar Telescope at Kitt Peak. The spectrometer parameters were described in the CuH paper (*16*).

III. RESULTS AND DISCUSSION

The fundamental band of NeH^+ was identified and assigned with the aid of the previous laser work (*3*). Additional transitions up to $J = 19$ were found. The (2, 1), (3, 2), (4, 3), and (2, 0) bands of $^{20}NeH^+$ were all searched for but only the (2, 1) and (3, 2) bands were found. The (4, 3) band was too weak to observe and the (2, 0) band lies higher than the 5000 cm^{-1} cutoff of the Ge filter. Since ^{22}Ne has an abundance of 8.8%, only the fundamental band of $^{22}NeH^+$ had a high enough signal-to-noise ratio to be recorded.

When H_2 was replaced by D_2 the (1, 0) and (2, 1) bands of $^{20}NeD^+$ were found. Unfortunately, the signal-to-noise ratio was not as high for $^{20}NeD^+$ as for $^{20}NeH^+$, preventing observation of $^{22}NeD^+$. The InSb detector allowed only lines with frequencies greater than 1800 cm^{-1} to be detected, so P lines of the (2, 1) band of $^{20}NeD^+$ were not detected.

TABLE IA

The Observed Line Positions for the Vibration–Rotation Spectra of ^{20}NeH$^+$ (in cm^{-1}) [The numbers in parentheses are observed-calculated line positions using the constants of Table II (in 10^{-4} cm^{-1})]

J	(1,0)		(2,1)		(3,2)	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
0	2710.3557(-2)d		a		2258.6751(1)	
1	2740.6262(5)d	2643.1910(-1)d	a	-	2284.6278(68)	2200.1589(31)
2	2768.6034(10)d	2606.4239(-4)d	2537.7239(27)	2386.3239(-19)	2308.2823(103)	2167.7094(-10)
3	2794.2240(2)d	2567.6203(-6)d	2561.2136(10)	b	2329.5719(92)	2133.2258(2)
4	2817.4273(-7)d	2526.8468(3)d	2582.2931(-8)	b	b	2096.7664(25)
5	2838.1535(-4)d	a	2600.9023(3)	2270.6280(-32)	2364.7986(1)	2058.3795(-77)
6	2856.3412(-2)d	2439.6492(14)	2616.9719(-20)	2228.3070(2)	2378.6015(-74)	2018.1436(111)
7	2871.9317(7)	2393.3598(41)	2630.4454(-9)	2184.2094(10)	2389.7925(33)	1976.1360(46)
8	2884.8650(13)	2345.3505(-59)	2641.2531(-25)	2138.4014(28)	2398.2653(-32)	1932.3739(29)
9	2895.0806(-7)	2295.7165(5)	a	2090.9395(4)	2403.9755(15)	1886.9359(37)
10	2902.5272(12)	2244.5066(70)	2654.6242(-26)	2041.8924(21)	2406.8165c	
11	2907.1418(19)	2191.7758(39)	2657.0578(4)	1991.3129(18)	2406.7743c	
12	2908.8693(39)	2137.6115(63)	2656.5624(8)	1939.2572(-14)	2403.6858(43)	
13	2907.6454(14)	2082.0202(-111)	2653.0680(-16)	1885.7912(40)	2397.5026(-71)	
14	2903.4178(18)	2025.1267(-120)	2646.5120(22)	1830.9424(-65)	2388.1580(28)	
15	2896.1078(-113)	1966.9797(72)	2636.8127(51)			
16	2885.6918(-3)	1907.5878(40)	2623.8822(33)			
17	2872.0690(49)	1847.0297(118)				
18	2855.1669(39)					
19	2834.9058(-36)					

a: obscured by an atomic line.
b: overlapped by CO$_2$ absorption.
c: badly blended and not included in the final fit.
d: These measurements are taken from the paper of Wong et al.(see text, Ref. 3).

Table IA contains the observed lines of the (1, 0), (2, 1), and (3, 2) bands of ^{20}NeH$^+$. Table IB has the (1, 0) and (2, 1) line positions for ^{20}NeD$^+$ as well as the (1, 0) lines for ^{22}NeH$^+$. The calibration of the lines is described in the CuH paper. The observed

TABLE IB

The Observed Line Positions for the Vibration–Rotation Spectra of ^{20}NeD$^+$ and ^{22}NeH$^+$ (The numbers in parentheses are observed-calculated line positions using the constants of Tables III and IV)

| J | ^{20}NeD$^+$ | | | ^{22}NeH$^+$ | |
| | (1,0) | | (2,1) | (1,0) | |
	R(J)	P(J)	R(J)	R(J)	P(J)
0	-		-	2704.8620(10)d	-
1	2018.776(-1)		-	2735.0111(-1)d	2637.9816(22)d
2	2034.598(8)	1947.105(-7)	1913.918(12)	2762.8834(-5)d	2601.3746(-24)d
3	2049.517(-9)	1927.175(-4)	1928.036(-2)	2788.4168(-2)d	2562.7479(1)d
4	2063.571(4)	1906.467(-8)	1941.283(2)	2811.5467(-25)d	2522.142c
5	2076.694(-4)	1885.027(8)	1953.630(13)	2832.225(5)	b
6	2088.897(-4)	1862.830(1)	1965.022(-8)	2850.364(-5)	2435.377(2)
7	2100.170(10)	1839.925(1)	1975.504(1)	2865.939(2)	2389.297(7)
8	2110.458(-2)		1985.018(0)	2878.874(8)	b
9	2119.772(-9)		1993.561(2)	2889.096(-3)	b
10	2128.109(-2)		2001.110(4)	2896.586(7)	2241.175(3)
11	2135.419(-14)		2007.628(-16)	a	
12	2141.737(6)		2013.154(-1)	2903.049(-4)	
13	2146.994(4)			2901.938(0)	
14	2151.198(5)				
15	2154.333(5)				
16	2156.367(-10)				
17	2157.332(6)				
18	2157.162(1)				
19	2155.855(-13)				
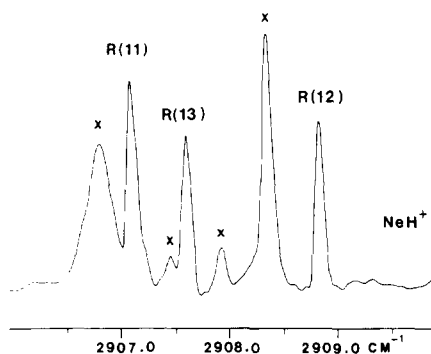
FIG. 1. The $R(11)$, $R(12)$, and $R(13)$ lines of fundamental band of $^{20}NeH^+$ at the bandhead. Lines marked with an X do not belong to NeH'.

linewidth of 0.095 cm^{-1} was determined by the instrumental resolution and some apodization required to suppress the ringing present in our under-resolved spectrum. The maximum signal-to-noise ratio was about 30 so the very strongest lines are accurate to 0.003 cm^{-1}. Figure 1 shows a portion of the spectrum near the (1, 0) R head. Our spectra contain a large number of lines from CO, H_2, OH, CO_2, and atomic lines which can overlap the NeH^+ lines of interest.

The lines of Table IA were simultaneously fit to the customary $^1\Sigma^+$ rotational energy expression (17). The molecular constants for $^{20}NeH^+$ are reported in Table II. Only one L parameter was required and we chose to determine L_0. The 11 lines of the fundamental $^{20}NeH^+$ band determined in the previous laser work are more accurate than our Fourier transform measurements, and so were weighed appropriately and used in our fits.

The lines of Table IB were treated in a similar fashion. The $^{22}NeH^+$ and $^{20}NeD^+$ data were much less extensive so the H values were not reliably determined. The H_v constants were fixed to values computed from corresponding $^{20}NeH^+$ constants using the ρ^6 isotopic dependence (17). The molecular constants for $^{20}NeD^+$ and $^{22}NeH^+$ are presented in Tables III and IV, respectively.

TABLE II

Molecular Constants (in cm^{-1}) for the Ground State of $^{20}NeH^+$

Molecular[a] Constants	v = 0	v = 1	v = 2	v = 3
T_v	0.0	2677.8565(5)	5131.2741(29)	7361.7726(35)
B_v	17.338053(74)	16.255055(56)	15.17667(10)	14.09358(14)
$10^3 D_v$	2.68550(83)	2.66071(51)	2.65233(79)	2.6723(15)
$10^8 H_v$	8.94(34)	7.80(13)	2.99(17)	-3.38(40)
$10^{11} L_v$	4.38(48)	-	-	-

a: The values in parentheses represent one standard deviation in the last digit.

TABLE III

Molecular Constants for the Ground State of ^{22}NeH⁺ (in cm⁻¹)

Molecular[a] Constants	v = 0	v = 1
T_v	0.0	2672.4960(10)
B_v	17.26360(19)	16.18779(16)
$10^3 D_v$	2.6615(15)	2.6386(11)
$10^8 H_v$	8.82[b]	7.70[b]

a: The values in parentheses represent one standard deviation in the last digit.
b: Fixed values (see text).

The simultaneous fitting of all vibration–rotation bands for all isotopes using Watson's modifications (*18, 19*) of Dunham's vibration–rotation energy expression is currently quite fashionable. We have fit all of the lines of Tables I [using a computer program supplied by Johns (*5*)] to produce the Dunham coefficients, Y_{kl}, the mass independent coefficients, U_{kl}, and the Watson Born–Oppenheimer breakdown parameters, Δ_{kl} (Table V). The quality of the fit is essentially the same as for the separate fits for each isotope.

The constants of Table V represent equilibrium molecular parameters and can be compared with theoretical predictions of Rosmus and Reinsch (*13*). The U_{01} parameter can be converted to $r_e^{BO} = 0.991195$ Å (*19*). The theoretical estimates of Rosmus and Reinsch (*13*) are $r_e = 0.996$ Å, $B_e = 17.72$ cm⁻¹, $\alpha_e = 1.096$ cm⁻¹, $\omega_e = 2896$ cm⁻¹, and $\omega_e x_e = 113$ cm⁻¹, in remarkable agreement with the constants of Table V.

It was noted by Warner *et al.* (*11*) for the protonated rare gases and by Tiemann and co-workers (*20*) for many other molecules that the Born–Oppenheimer breakdown parameters often vary in a systematic way. For instance, $\Delta_{01}^H = 0.176(77)$ for NeH⁺ while $\Delta_{01}^H = 0.1244(37)$ and $0.1215(40)$ for ArH⁺ and KrH⁺, respectively. Also, $\Delta_{10}^{Ar} = 0.73(14)$ for ArH⁺ and $\Delta_{10}^{Ne} = 0.78(25)$ for NeH⁺, but the other parameters for NeH⁺ are not similar to the corresponding ArH⁺ parameters.

In conclusion, Fourier transform spectroscopy has the sensitivity to detect the vi-

TABLE IV

Molecular Constants for the Ground State of ^{20}NeD⁺ (in cm⁻¹)

Molecular[a] Constants	v = 0	v = 1	v = 2
T_v	0.0	1984.5937(33)	3850.9445(103)
B_v	9.17031(28)	8.75811(32)	8.34852(38)
$10^3 D_v$	0.7404(41)	0.7339(35)	0.7307(30)
$10^8 H_v$	1.29[b]	1.12[b]	0.43[b]

a: The values in parentheses represent one standard deviation in the last digit.
b: Fixed values (see text).

TABLE V

Dunham Coefficients for the Ground State of $^{20}NeH^+$ (U's are in cm^{-1} $amu^{(k/2+1)}$ and Y's are in cm^{-1})

k	l	U_{kl}	Y_{kl}
1	0	2846.141(23)[a]	2903.751[b]
2	0	-109.1780(71)	-113.3581
3	0	0.2378(11)	0.2530
0	1	17.15846(72)[c]	17.88472
1	1	-1.02947(25)	-1.09678
2	1	$0.862(14) \times 10^{-2}$	0.937×10^{-2}
3	1	$-0.1404(22) \times 10^{-2}$	-0.1557×10^{-2}
0	2	$-0.24986(11) \times 10^{-2}$	-0.271403×10^{-2}
1	2	$0.346(13) \times 10^{-4}$	0.383×10^{-4}
2	2	$-0.245(65) \times 10^{-5}$	-0.278×10^{-5}
3	2	$-0.1348(83) \times 10^{-5}$	-0.1558×10^{-5}
0	3	$0.1444(45) \times 10^{-6}$	0.1635×10^{-6}
1	3	$-0.156(23) \times 10^{-7}$	-0.180×10^{-7}
2	3	$-0.625(73) \times 10^{-8}$	-0.738×10^{-8}
0	4	$-0.587(86) \times 10^{-10}$	-0.693×10^{-10}

a: The errors quoted in parentheses are one standard deviation in the last digit.
b: The following Δ values are also required to fit the observed isotopic lines:

$$\Delta_{10}^{Ne} = 0.78(25) \qquad \Delta_{10}^{H} = -1.2159(81) \qquad \Delta_{20}^{H} = -6.945(93)$$

$$\Delta_{01}^{H} = 0.176(77) \qquad \Delta_{11}^{H} = 2.38(21)$$

The listed Y_{kl} values are for $^{20}NeH^+$. Notation is the same as in Ref. 5.
c: The value of equilibrium internuclear distance deduced from U_{01} is 0.991195(21) Å.

bration–rotation spectra of molecular ions. A large number of lines from several bands of $^{20}NeH^+$, $^{22}NeH^+$, and $^{20}NeD^+$ were detected. Molecular parameters, including Born–Oppenheimer breakdown parameters, were extracted from the data. For $^{20}NeH^+$ the energy levels cover the potential curve nearly half way to dissociation (13).

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