

# Observation of the infrared absorption spectra of $^{20}\text{NeH}^+$ and $^{22}\text{NeH}^+$ with a difference frequency laser

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The fundamental bands of  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  in the region around  $3.7\ \mu\text{m}$  have been observed in absorption. The wave numbers of 11 transitions of  $^{20}\text{NeH}^+$  and 8 transitions of  $^{22}\text{NeH}^+$  have been measured, from which we obtain the following molecular parameters (in  $\text{cm}^{-1}$ , three standard deviations in parentheses):

	$^{20}\text{NeH}^+$	$^{22}\text{NeH}^+$
$\nu_0$	2677.856 4(13)	2672.497 1(15)
$B_0$	17.338 21(28)	17.263 69(32)
$(B_1 - B_0)$	-1.082 96(18)	-1.075 95(26)
$D_0 \times 10^3$	2.692(15)	2.664(19)
$(D_1 - D_0) \times 10^3$	-0.023 5(72)	-0.023 2(72)

The equilibrium molecular constants  $B_e$ ,  $\alpha_e$ ,  $D_e$ ,  $\beta_e$ ,  $\omega_e$ ,  $\omega_e X_e$ , and  $r_e$  have also been derived.

## I. INTRODUCTION

Recently, the infrared fundamental band of  $\text{HeH}^+$  has been detected in absorption<sup>1</sup> using a difference frequency laser system<sup>2</sup> and a multiple-reflection discharge cell. This technique was developed by Oka to observe the vibration-rotation spectrum of  $\text{H}_3^+$ .<sup>3</sup>

In the present paper, we report the observation of the fundamental bands of  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  (8.8% natural abundance). Our observations represent the first high resolution spectroscopic detection of these molecular ions.

A number of *ab initio* calculations have been performed on  $\text{NeH}^{+6-8}$  and the high quality CEPA calculations of Rosmus and Reinsch<sup>8</sup> provided good estimates of the molecular constants which greatly alleviated our search problem. Estimates for the molecular constants of the protonated rare gases are also available from a number of experiments such as beam scattering<sup>4</sup> or associative ionization,<sup>5</sup> but the accuracy of these estimates is low.

Eleven transitions  $P(4)$  to  $R(6)$  in the fundamental band of  $^{20}\text{NeH}^+$  and eight transitions  $P(3)$  to  $R(4)$  of  $^{22}\text{NeH}^+$  have been observed. Accurate molecular constants have been determined for the ground and first excited vibrational states of each isotopic species and from these parameters equilibrium molecular constants have been derived.

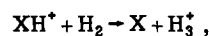
The observed transition frequencies may prove useful for the infrared detection of  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  in the interstellar medium.

## II. EXPERIMENTAL

The difference frequency infrared laser system and multiple-reflection discharge cell used in the present study has been described by Oka<sup>3</sup>; minor changes have been made by Bernath and Amano.<sup>1</sup> Briefly, several  $\mu\text{w}$  of tunable infrared radiation were generated by mixing the output of a cw dye laser with that of a single mode argon ion laser. The laser beam was passed 16

times through the ice-cooled discharge cell for a total path length of 32 m. The infrared source was frequency modulated at 2.5 kHz and the absorption signal and the reference signal were demodulated with  $2f$  and  $1f$  phase sensitive detection, respectively. The reference gases used for infrared frequency calibration were  $\text{H}_2\text{CO}$ ,<sup>9</sup>  $\text{H}_2\text{S}$ ,<sup>10</sup> and  $\text{N}_2\text{O}^{11}$ ; the absolute accuracy of the frequency standards employed should be about  $\pm 0.0005\ \text{cm}^{-1}$ . Our frequency measurements, which were based on linear interpolation with markers at 300 MHz intervals, had a comparable uncertainty. We estimate that the absolute accuracy of the  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  measurements is about  $\pm 0.001\ \text{cm}^{-1}$ .

It was noted by Bernath and Amano<sup>1</sup> in their detection of  $\text{HeH}^+$  that a dilute mixture (1:100) of  $\text{H}_2$  in He should be used for the optimum signal. Brault and Davis also recognized that very little  $\text{H}_2$  was necessary in their study of  $\text{ArH}^+$  by infrared emission<sup>12</sup> and we find that this is also the case for  $\text{NeH}^+$ . This general characteristic of  $\text{HeH}^+$ ,  $\text{NeH}^+$ , and  $\text{ArH}^+$  ions is due to the fast reaction<sup>13</sup>



which removes  $\text{XH}^+$ . Before searching for  $\text{NeH}^+$ , we detected the transition  $R(5)$  of  $\text{ArH}^+$  (at  $2696.3731\ \text{cm}^{-1}$ ),<sup>12</sup> as well as the transition  $P(2)$  of  $\text{HeH}^+$  (at  $2771.8059\ \text{cm}^{-1}$ )<sup>1</sup> in order to establish favorable experimental conditions for  $\text{NeH}^+$ .

The theoretical calculations of Rosmus and Reinsch<sup>8</sup> predict the band origin to be at  $2670 \pm 20\ \text{cm}^{-1}$ . With ice-water cooling, the  $\text{NeH}^+$  rotational temperature was expected to be about 450 K. Therefore, the maximum absorption should occur at  $R(2)$  or  $R(3)$ . On the basis of these considerations, the infrared frequency was scanned from 2733 up to 2772  $\text{cm}^{-1}$  in  $1\ \text{cm}^{-1}$  intervals. The scanning speed was  $\sim 0.5\ \text{cm}^{-1}/\text{min}$  with a time constant of 400 ms and the overall sensitivity of the search was  $1 \times 10^{-5} - 1 \times 10^{-6}\ \text{cm}^{-1}$ . Four lines were found in the above frequency range and they were identified as the  $R(1)$  and  $R(2)$  transitions of  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  from the frequency spacings and relative intensities. The

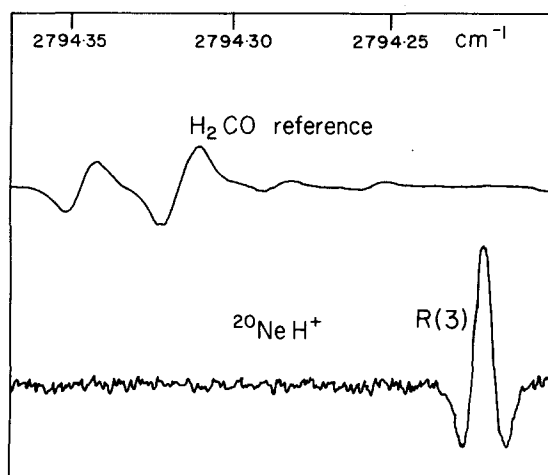


FIG. 1. The  $R(3)$  line of the  $\nu=1-0$  band of  $^{20}\text{NeH}^+$  at  $2794.2240\text{ cm}^{-1}$  in absorption obtained with frequency modulation and  $2f$  phase sensitive detection. The reference lines of  $\text{H}_2\text{CO}$  were taken simultaneously with  $1f$  phase sensitive detection. The time constants were  $0.125\text{ s}$ .

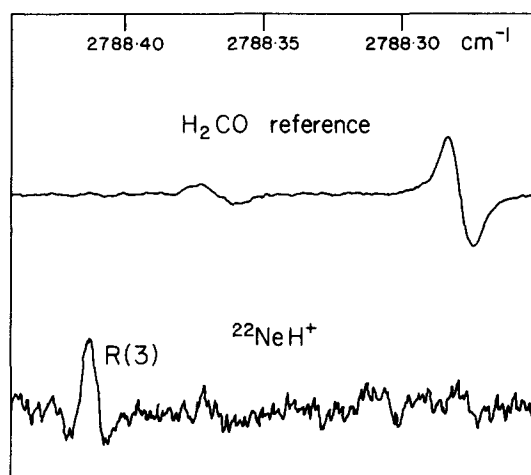


FIG. 2. The  $R(3)$  line of the  $\nu=1-0$  band of  $^{22}\text{NeH}^+$  at  $2788.4168\text{ cm}^{-1}$  in absorption obtained under similar conditions as Fig. 1 except that the time constants were  $0.4\text{ s}$ .

optimum current density was found to be about  $30\text{ mA/cm}^2$  with a Ne pressure of  $160\text{ Pa}$ . The optimum signal was obtained when no  $\text{H}_2$  was added to the Ne sample. Evidently, the hydrogen (as  $\text{H}_2\text{O}$ , etc.) which was present as an impurity in the Ne sample or in the discharge cell was sufficient to generate the required concentration of  $\text{NeH}^+$  ions. The sample of Ne (99.99% minimum purity) was supplied by Matheson.

### III. RESULTS AND ANALYSIS

#### A The observed spectra of $^{20}\text{NeH}^+$ and $^{22}\text{NeH}^+$

Sections of the observed absorption spectra of  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  are shown in Figs. 1 and 2. The strongest observed line  $R(3)$  of  $^{20}\text{NeH}^+$  is illustrated in Fig. 1 along with the nearby  $\text{H}_2\text{CO}$  reference lines. Figure 2 is a trace of the line  $R(3)$  of  $^{22}\text{NeH}^+$ . Table I lists the wave numbers of the observed transitions.

The lines observed for  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  had a Doppler width (HWHM) of about  $140\text{ MHz}$ , which corresponds to a translational temperature of about  $500\text{ K}$ . However,

from the relative intensities of the transitions the rotational temperature was estimated to be about  $700\text{ K}$ . For the  $R(4)$  line of  $^{20}\text{NeH}^+$ , the absorption (in a path length of  $32\text{ m}$ ) was measured by amplitude modulation to be about  $7.3\%$ . Using the transition dipole moment from the *ab initio* calculation of Rosmus and Reinsch<sup>8</sup> and the molecular constants determined in this work, we estimate the average concentration of  $^{20}\text{NeH}^+$  to be about  $2 \times 10^{10}\text{ molecules/cm}^3$ .

#### B Determination of the molecular parameters

The vibration-rotation term values of a  $^1\Sigma$  state are given by

$$F_v(J) = T_v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 \quad (1)$$

and the transition wave numbers in the  $\nu=1-0$  band by

$$\nu(m) = \nu_0 + \nu_r(m), \quad (2a)$$

where

$$\nu_0 = T_1 - T_0, \quad (2b)$$

TABLE I. Observed wave numbers (in  $\text{cm}^{-1}$ ) for the fundamental bands of  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  (Obs. - Calc. in units of  $10^{-4}\text{ cm}^{-1}$ ).

Transition	$^{20}\text{NeH}^+$		$^{22}\text{NeH}^+$	
	Obs.	Obs. - Calc. <sup>a</sup>	Obs.	Obs. - Calc. <sup>a</sup>
$R(6)$	2856.3412	0	...	...
$R(5)$	2838.1535	2	...	...
$R(4)$	2817.4273	-4	2811.5467	-4
$R(3)$	2794.2240	0	2788.4168	10
$R(2)$	2768.6034	4	2762.8834	-3
$R(1)$	2740.6262	0	2735.0111	-7
$R(0)$	2710.3557	-5	2704.8620	0
$P(1)$	2643.1910	3	2637.9816	12
$P(2)$	2606.4239	1	2601.3746	-12
$P(3)$	2567.6203	-4	2562.7479	3
$P(4)$	2526.8468	0	...	...

<sup>a</sup>Calculated with the constants of Table II.

$$\begin{aligned} \nu_r(m) = & 2B_0m + (B_1 - B_0)m(m+1) - 4D_0m^3 \\ & - (D_1 - D_0)m^2(m+1)^2 + 2H_0m^3(3m^2 + 1) \\ & + (H_1 - H_0)m^3(m+1)^3, \end{aligned} \quad (2c)$$

and  $m$  is a running index with  $m = -J$  for  $P$ -branch lines and  $m = J+1$  for  $R$ -branch lines. The least-squares fit was made using Eq. (2).

In preliminary least-squares fits of the  $^{20}\text{NeH}^+$  data, the parameters  $H_1$  and  $H_0$  could not be determined. However, a reliable estimate for  $H_e$  can be made by using the equation<sup>14,16</sup>

$$H_e = \frac{2D_e}{3\omega_e} (12B_e^2 - \alpha_e\omega_e), \quad (3)$$

where the subscript  $e$  indicates equilibrium values. For  $\text{HeH}^+$  and  $\text{ArH}^+$ ,<sup>12</sup> the above equation was found to give  $H_e$  within 10% of the experimental values. For  $^{20}\text{NeH}^+$ ,  $H_e$  was calculated to be  $1.5 \times 10^{-7} \text{ cm}^{-1}$  from preliminary molecular constants. At the highest  $J$  concerned ( $J=6$ ), the contribution of the fifth term in Eq. (2c) due to  $H_0 \approx H_e$  is about  $0.01 \text{ cm}^{-1}$ . Thus, although  $H_0$  could not be determined from the data in Table I it should not be neglected. Since  $(H_1 - H_0)$  is likely to be less than 10% of  $H_e$ , we neglected the vibrational dependence of  $H_e$ .

For  $^{22}\text{NeH}^+$ , the first four parameters of Eq. (2), namely  $\nu_0$ ,  $B_0$ ,  $(B_1 - B_0)$ , and  $D_0$ , were adequate to give an acceptable fit but  $(D_1 - D_0)$  could not be determined. The parameter  $(D_1^i - D_0^i) \cong \beta_e^i$  of  $^{22}\text{NeH}^+$  is related to the parameter  $(D_1 - D_0)$  of  $^{20}\text{NeH}^+$  by the isotopic relationship<sup>14</sup>

$$(D_1^i - D_0^i) = \rho^5 (D_1 - D_0), \quad (4)$$

where  $\rho = \sqrt{\mu/\mu^i}$ ,  $\mu$ , and  $\mu^i$  are the charge-modified reduced masses<sup>15</sup> of  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$ , respectively. The parameters for  $^{22}\text{NeH}^+$  are distinguished with a superscript  $i$  whenever necessary. The final least-squares fit was carried out using Eq. (4) as a constraint and with  $H_1$  and  $H_0$  fixed at  $1.50 \times 10^{-7} \text{ cm}^{-1}$  for  $^{20}\text{NeH}^+$  and  $1.48 \times 10^{-7} \text{ cm}^{-1}$  for  $^{22}\text{NeH}^+$ . The values of the parameters and their uncertainties are given in Table II. The residuals, (obs. - calc.), of the fit are given in Table I. The rms deviations for  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  are  $0.0003$  and  $0.0008 \text{ cm}^{-1}$ , respectively. The introduction of  $H_0$  into the fit had little effect on  $\nu_0$ ,  $B_0$ ,  $(B_1 - B_0)$ , and  $D_0$ , but the parameter  $(D_1 - D_0)$  changed by about

TABLE II. The molecular constants of the fundamental bands of  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$  (in  $\text{cm}^{-1}$ ).<sup>a</sup>

	$^{20}\text{NeH}^+$	$^{22}\text{NeH}^+$
$\nu_0$	2677.856 4(13)	2672.497 1(15)
$B_0$	17.338 21(28)	17.263 69(32)
$(B_1 - B_0)$	-1.082 96(18)	-1.075 95(26)
$D_0 \times 10^3$	2.692 (15)	2.664(19)
$(D_1 - D_0) \times 10^3$	-0.023 5(72)	-0.023 2(72)
$H_0 \times 10^7$ <sup>b</sup>	1.50	1.48
$(H_1 - H_0)$ <sup>b</sup>	0.0	0.0

<sup>a</sup>Errors are three standard deviations.

<sup>b</sup>Fixed. See the text for details.

TABLE III. The equilibrium molecular constants<sup>a</sup> of  $^{20}\text{NeH}^+$  and  $^{22}\text{NeH}^+$ .<sup>b</sup>

	$^{20}\text{NeH}^+$		$^{22}\text{NeH}^+$
	Expt.	Calc. <sup>c</sup>	Expt.
$B_e$	17.88(2)	17.72	17.80(2)
$\alpha_e$	1.08(4)	1.096	1.08(4)
$D_e \times 10^3$	2.704 (17) <sup>d</sup>	...	2.676 (19)
$\beta_e \times 10^3$	-0.023 5(72) <sup>d</sup>	...	-0.023 2(72)
$\omega_e$	2900(6)	2896	2894(6)
$\omega_e x_e$	111(6)	113	111(6)
$r_e$	0.991 3(6)	0.996	0.991 3(6)

<sup>a</sup>As defined in Eqs. (5)–(9).

<sup>b</sup>All units are in  $\text{cm}^{-1}$  except  $r_e$  which is in Å.

<sup>c</sup>CEPA calculations of Ref. 8.

<sup>d</sup>Uncertainties for  $D_e$  and  $\beta_e$  are three standard deviations, all other uncertainties are estimated in the text.

three times the standard deviation. This correlation between  $H_0$  and  $(D_1 - D_0)$  was not unexpected as they are both determined by the higher  $J$  transitions.

### C Estimation of equilibrium molecular constants

While the Born–Oppenheimer approximation holds quite well for heavy molecules, it begins to break down for lighter molecules and higher order corrections must be considered in obtaining the equilibrium constants. Even for a diatomic molecule, it is a difficult task to study these higher order corrections as this requires a knowledge of precisely measured molecular constants of the molecule in several vibrational levels. In addition, this information is required for two or more isotopically substituted molecules with each atom substituted at least once.<sup>15</sup> Although we have data for two isotopic species in two vibrational levels, the data are insufficient to observe the breakdown of the Born–Oppenheimer approximation.

We define the equilibrium molecular constants to be as given by the following equations<sup>14</sup>:

$$B_0 = B_e - 0.5\alpha_e + 0.25\gamma_e + \dots, \quad (5)$$

$$B_1 - B_0 = -\alpha_e + 2\gamma_e + \dots, \quad (6)$$

$$D_0 = D_e + 0.5\beta_e + \dots, \quad (7)$$

$$D_1 - D_0 = \beta_e + \dots, \quad (8)$$

$$\nu_0 = \omega_e - 2\omega_e x_e + 3.25\omega_e y_e + 5\omega_e z_e + \dots. \quad (9)$$

The constant  $B_e$  and  $\alpha_e$  were derived from Eqs. (8) and (9) by neglecting  $\gamma_e$  and higher order terms. An estimate of the size of  $\gamma_e$  is available from  $\gamma_e \sim (B_e/\omega_e)\alpha_e = 0.007 \text{ cm}^{-1}$ , the neglect of  $\gamma_e$  thus would result (conservatively) in an error of about  $0.04 \text{ cm}^{-1}$  in  $\alpha_e$  and  $0.02 \text{ cm}^{-1}$  in  $B_e$ . The equilibrium bond length was calculated from  $B_e$  without further corrections. The corresponding isotopic equation for Eq. (9) is

$$\nu_0^i = \rho\omega_e - 2\rho^2\omega_e x_e + 3.25\rho^3\omega_e y_e + 5\rho^4\omega_e z_e. \quad (10)$$

Neglecting  $\omega_e y_e$  and  $\omega_e z_e$  in Eqs. (9) and (10) results in

$\omega_e = 2900(6)$  and  $\omega_e x_e = 111(6)$   $\text{cm}^{-1}$  for  $^{20}\text{NeH}^+$ . The equilibrium constants are summarized in Table III.

#### IV. DISCUSSION

The experimental equilibrium molecular constants for the protonated rare gas ions test the quality of the *ab initio* predictions. Table III shows a comparison of our experimental constants for  $\text{NeH}^+$  with the theoretical results of Rosmus and Reinsch.<sup>8</sup> Our observed constants are in good agreement with the calculated values.

The technique of difference frequency laser spectroscopy has considerable potential for the systematic study of electrical discharges. Translational and rotational temperatures as well as average ion concentrations are easily measured. It is interesting to compare the behavior of  $\text{HeH}^+$ ,  $\text{NeH}^+$ , and  $\text{ArH}^+$  from the limited available data. At the same discharge current of 140 mA and with liquid  $\text{N}_2$  cooling for  $\text{HeH}^+$  and ice-water cooling for  $\text{NeH}^+$  and  $\text{ArH}^+$ , the translational temperatures of  $\text{HeH}^+$ ,  $\text{NeH}^+$ , and  $\text{ArH}^+$  are 200, 500, and 740 K, respectively, and the estimated ion densities are  $7 \times 10^9$ ,  $2 \times 10^{10}$ , and  $9 \times 10^{10}$  molecules/ $\text{cm}^3$ , respectively. These variations between the ions could be due to differences in the reaction kinetics. A systematic study of the effective translational, rotational and vibrational temperatures from the linewidths and intensities of the fundamental and hot bands with respect to discharge current and mixing ratios of the neutral species could help to check ion-molecule reaction schemes and electrical discharge theories.

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- <sup>1</sup>P. Bernath and T. Amano, *Phys. Rev. Lett.* **48**, 20 (1982).
- <sup>2</sup>A. S. Pine, *J. Opt. Soc. Am.* **64**, 1683 (1974); **66**, 97 (1976).
- <sup>3</sup>T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980).
- <sup>4</sup>H. Weise, H. Mittmann, A. Ding, and A. Henglein, *Z. Naturforsch. Teil A* **26**, 1122 (1971); W. B. Rich, S. M. Bobbio, R. L. Champion, and L. D. Doverspike, *Phys. Rev. A* **4**, 2253 (1971).
- <sup>5</sup>J. Lorenzen, H. Hotop, M. W. Ruf, and M. Morgner, *Z. Phys. A* **297**, 19 (1980).
- <sup>6</sup>S. Peyerimhoff, *J. Chem. Phys.* **43**, 998 (1965).
- <sup>7</sup>V. Bondybey, P. K. Pearson, and H. F. Schaefer III, *J. Chem. Phys.* **57**, 1123 (1972).
- <sup>8</sup>P. Rosmus and E. A. Reinsch, *Z. Naturforsch. Teil A* **35**, 1066 (1980).
- <sup>9</sup>A. S. Pine, MIT Lincoln Laboratory Report No. NSF/ASRA/DAR-78-24 562, 1980.
- <sup>10</sup>J. W. C. Johns (private communication).
- <sup>11</sup>C. Amiot and G. Guelachvili, *J. Mol. Spectrosc.* **59**, 171 (1976); C. Amiot, *ibid.* **59**, 191 (1976).
- <sup>12</sup>J. W. Brault and S. P. Davis, *Phys. Scr.* **25**, 26 (1982).
- <sup>13</sup>D. K. Bohme, G. I. Mackay, and H. I. Schiff, *J. Chem. Phys.* **73**, 4976 (1980).
- <sup>14</sup>G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950).
- <sup>15</sup>J. K. G. Watson, *J. Mol. Spectrosc.* **80**, 411 (1980).
- <sup>16</sup>J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).