NOTES

The Pure Rotational Spectrum of ArH+ [1]

The protonated rare gas molecules have been shown to be comparatively stable ions and quite high concentrations of them ($\sim 10^{10}$–10^{11} molecules cm^{-3}) can be formed in electric discharges through appropriate gas mixtures (*1*). We report here the observation of lines in the pure rotational spectrum of ArH+ in its ground vibrational level, recorded using tunable far-infrared radiation (*2*).

The molecule was first detected spectroscopically by Brault and Davis (*3*), who observed bands in the vibration–rotation spectrum in emission with a Fourier transform interferometer. These observations were later extended to higher vibrational levels by Johns (*4*). Bowman *et al.* (*5*) measured the frequencies of the $J = 1$–0 pure rotational lines of $^{40}ArD^+$, $^{38}ArD^+$, and $^{36}ArD^+$ in the millimeter-wave region of the spectrum. Very recently, the $J = 1$–0 transition in ArH+ and the $J = 2$–1 transition in ArD+ (both around 616 GHz) have been studied in a magnetic field with a tunable far-infrared source by Laughlin *et al.* (*6*). The measurement of the isotopic dependence of the rotational g factor allowed them to estimate the electric dipole moment as 1.4 ± 0.4 D (measured relative to the center of mass).

In our experiments, coherent, tunable far-infrared radiation was generated by nonlinear mixing of the radiation from two CO_2 lasers in a metal–insulator–metal diode (*2*). Details of the spectrometer have been given elsewhere (*7*). The far-infrared radiation made a single pass through a copper hollow cathode discharge tube, in which the ions were created, and was detected with a helium-cooled bolometer. The tube was 14 mm i.d. and 3.9 m long, with eight anodes uniformly distributed along its length. A dc discharge was passed through a flowing mixture of 100 ppm of hydrogen in argon at a total pressure of about 95 Pa (700 mTorr). The discharge tube was cooled by filling an insulating jacket which surrounded it with liquid nitrogen. The optimum signal for ArH+ was obtained with a total discharge current of 350 mA. A recording of the $J = 6 \leftarrow 5$ transition at 3.68 THz is shown in Fig. 1. The first-derivative lineshape results from the use of frequency modulation (in this case at 1 kHz with a depth of 8 MHz).

Six rotational transitions of ArH+ in its ground vibrational state were detected in this way. The measured frequencies are given in Table I. The high quality of the previous Fourier transform work (*3, 4*) was immediately obvious because our measured values were within 2–3 MHz of the values predicted using their parameters. The frequency of a pure rotational transition $J + 1 \leftarrow J$ of a molecule in a $^1\Sigma$ state is given by
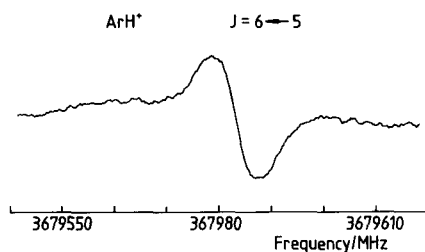

ArH*   J = 6 ⟵ 5

3679550   367980   3679610
Frequency/MHz

FIG. 1. An experimental recording of the $J = 6 \leftarrow 5$ rotational transition of ArH+ in its ground vibrational level. The signal appears as the first derivative of an absorption curve because the far-infrared radiation is frequency modulated at 1 kHz. The signal was detected with a lock-in amplifier, with an output time constant of 400 msec.

TABLE I

The Pure Rotational Spectrum of ArH$^+$ in the $v = 0$ Level of the $X^1\Sigma^+$ State:
Measured Frequencies and Molecular Parameters

Transition J	Observed Frequency (MHz)	Uncertainty (MHz)	Obs. − Calc.[a] (MHz)
1 ← 0	615858.4[b]	0.40	0.28
2 ← 1	1231271.18	0.30	0.21
3 ← 2	1845793.67	0.20	0.03
4 ← 3	2458981.89	0.35	0.01
5 ← 4	3070392.15	0.30	−0.32
6 ← 5	3679583.52	0.35	−0.03
7 ← 6	4286115.04	0.25	0.09
21 ← 20	12258483[c]	50	−14
22 ← 21	12774366[c]	50	−39
23 ← 22	13281119[c]	50	35

[a] Calculated value obtained using the values in Table II.
[b] Value measured during the course of the work described in Ref. (6).
[c] Value obtained by diode laser measurements (8).

$$v = 2B(J + 1) - 4D(J + 1)^3 + 6H(J + 1)^3[(J + 1)^2 + \tfrac{1}{3}] + 8L(J + 1)^5[(J + 1)^2 + 1] + \cdots \qquad (1)$$

in the usual terminology. We have used the frequencies measured in our work together with the other available rotational frequencies for ArH$^+$ to refine its rotational and centrifugal distortion parameters. The additional frequencies are those of the 1 ← 0 transition, measured by Laughlin *et al.* during the course of their work on the dipole moment (6), and of three high-J transitions recently measured in the infrared by Liu *et al.* (8) with a diode laser. The frequencies and their experimental uncertainties are given in Table I.

TABLE II

Rotational Parameters (in MHz) for ArH$^+$ in the $v = 0$ level of the $X^1\Sigma^+$ State

Parameter	Present work	Johns (4)
B	307966.169(68)[a]	307966.02(56)
D	18.5564(10)	18.5549(20)
$10^3 H$	0.4726(27)	0.4727(45)
$10^7 L$	− 0.2132[b]	− 0.213(36)

[a] The figures in parentheses represent one standard deviation of the least-squares fit, in units of the last quoted decimal place.
[b] Parameter constrained to this value, taken from Ref. (4).

The parameters in Eq. (1) were fitted to this data set, each measurement being weighted inversely as the square of the estimated uncertainty. The octic centrifugal distortion parameter L was not determinable in this way and was therefore constrained to the value determined by Johns (4). The quality of the least-squares fit was slightly better than the estimated experimental uncertainty (see Table I). The parameter values obtained in the fit are given in Table II and, as expected, are in excellent agreement with those of Johns.

The present measurements on ArH^+ give one considerable confidence in the molecular parameters determined from the Fourier transform studies (3, 4). Consequently, there is little point in measuring rotational transition frequencies for vibrationally excited ArH^+ even though such observations would be quite possible. Instead, we intend to study the far-infrared spectra of more elusive ions such as NeH^+, HeH^+, and H_2D^+.

ACKNOWLEDGMENTS

REFERENCES

1. M. WONG, P. BERNATH, AND T. AMANO, *J. Chem. Phys.* **77**, 643–696 (1982).
2. K. M. EVENSON, D. A. JENNINGS, AND F. R. PETERSEN, *Appl. Phys. Lett.* **44**, 576–578 (1984).
3. J. W. BRAULT AND S. P. DAVIS, *Phys. Scr.* **25**, 268–271 (1982).
4. J. W. C. JOHNS, *J. Mol. Spectrosc.* **106**, 124–133 (1984).
5. W. C. BOWMAN, G. M. PLUMMER, E. HERBST, AND F. C. DE LUCIA, *J. Chem. Phys.* **79**, 2093–2095 (1983).
6. K. B. LAUGHLIN, G. A. BLAKE, R. C. COHEN, D. C. HOVDE, AND R. J. SAYKALLY, *Phys. Rev. Lett.* **58**, 996–999 (1987).
7. D. A. JENNINGS, K. M. EVENSON, L. R. ZINK, C. DEMUYNCK, J. L. DESTOMBES, B. LEMOINE, AND J. W. C. JOHNS, *J. Mol. Spectrosc.* **122**, 477–480 (1987).
8. D. J. LIU, W. C. HO, AND T. OKA, *J. Chem. Phys.* **87**, 2442–2446 (1987).

JOHN M. BROWN

Physical Chemistry Laboratory
South Parks Road
Oxford OX1 3QZ, England

D. A. JENNINGS
M. VANEK
L. R. ZINK
K. M. EVENSON

National Bureau of Standards
Boulder, Colorado 80303
Received October 5, 1987