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Experimental determination of dipole moments for molecular ions: Improved measurements for ArH⁺

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An improved value for the dipole moment of ArH⁺ has been obtained from new measurements of the rotational *g* factors of ArH⁺ and ArD⁺ made with tunable far-IR laser spectroscopy. Systematic errors present in earlier measurements have been eliminated. The new result ($\mu = 3.0 \pm 0.6$ D) is slightly higher than the *ab initio* value of Rosmus (2.2 D) at the 2σ limits of precision.

INTRODUCTION

We have recently reported the development of a method for experimentally determining the dipole moments of molecular ions.^{1,2} By measuring the rotational *g* factors for two different isotopomers, the electric dipole moment can be calculated from the equation

$$\mu = -(eh/16\pi^2 M_p \Delta z) [(g'_r/B') - (g_r/B)] + Qe\Delta z/2, \quad (1)$$

where μ is the dipole moment of unsubstituted (unprimed) isotopomer, M_p is the mass of the proton, $\Delta z = z'_{c.m.} - z_{c.m.}$ is the shift in center of mass upon isotopic substitution, g_r is the rotational *g* factor, B is the rotational constant, and Q is the net charge on the molecule. The theory relating the dipole moment to the rotational *g* factors was first derived by Townes *et al.*,³ and was subsequently used to determine the sign of the dipole moment of CO.⁴ The conventional method for determination of dipole moments via observation of the Stark effect is clearly difficult to apply to molecular ions because of the translational motion of net charges induced by an electric field. However, observation of the rotational Zeeman effect of ions is actually convenient because the application of an axial magnetic field enhances the ion concentration in abnormal glow discharges used for molecular ion spectroscopy.⁵

In our initial demonstration of this method we have determined the dipole moment of ArH⁺. Our resulting experimental value [1.4 ± 0.4 (1σ)] agreed only very marginally with the *ab initio* result of Rosmus (2.2 D),⁶ but the uncertainty in our result was large and we suspect that systematic errors were present. In that work, rotational spectra of ArH⁺ and ArD⁺ were recorded using a tunable far-infrared (FIR) laser spectrometer, and the discharge was confined inside of a solenoid capable of producing magnetic fields up to 4 kG. In this paper, we present improved values for the rotational *g* factors resulting from refinements of the experimental technique. The basic approach is similar, but several important steps were taken to reduce both random and systematic errors. The new results are in clear disagreement with our earlier determination.^{1,2} Systematic errors present in the previous data set have been discovered and eliminated in the new measurements.

EXPERIMENTAL

Spectrometer

A tunable FIR laser spectrometer was used to record the data. Details of the construction and operation have been presented in Ref. 2, 7, and 8, and only the basic features are described here. A 150 W CO₂ laser (Apollo No. 150) optically pumps a FIR gas laser to produce nontunable FIR radiation at frequencies ranging from 300–6000 GHz. The FIR laser output is focused onto a corner cube mixer containing a GaAs Schottky barrier diode. Tunable microwave radiation from 2–75 GHz is also coupled onto the diode, and the sidebands at $\nu_{\text{Laser}} \pm \nu_{\text{MW}}$ which result from the nonlinear mixing process are reradiated back along the path of the incoming laser beam. The tunable sidebands are separated from the dominant laser carrier by a polarizing diplexer, and pass through the discharge cell to an InSb detector (Cochise Instruments).

Using the very strong 433 μm HCOOH FIR laser line, the system has produced an estimated single sideband power of 80 μW . For the ArH⁺ and ArD⁺ spectra presented here, the 513 μm HCOOH laser line was used, capable of producing 13 μW of single sideband power. The ArH⁺ $J = 1 \leftarrow 0$ absorption line at 615.858 GHz was observed using microwave power at 31.470 GHz, generated by frequency doubling the output of the fundamental microwave source (HP No. 8673B, 2–26.5 GHz) with a Spacek Ka-2X doubler, followed by amplification using a traveling wave tube (TWT) amplifier (Hughes No. 8001H12). The ArD⁺ $J = 2 \leftarrow 1$ absorption at 634.653 GHz was recorded with microwave power at 50.266 GHz, generated by passing the output of the TWT, as described above, into a second frequency doubler (Honeywell No. V2200N). The expanded microwave coverage allowed tunable FIR radiation to be produced for both the ArH⁺ and ArD⁺ spectra using lowest order sidebands.

Frequency modulation of the microwave source was used to detect the ion signals, with lock-in detection at twice the modulation frequency. A PDP 11/53 computer was used to store the spectra. Each scan was least-squares fitted to a sum of 2 derivative Lorentzian line shapes. Microwave scans of increasing and decreasing frequency were performed sequentially, and the average splitting was used in order to cancel the linear drift in the FIR laser frequency.

Magnet and discharge cell

A new magnet was constructed for the experiment presented here. Liquid nitrogen cooling of the copper wire was used to decrease the resistance of the solenoid by a factor of 9. Rectangular wire (0.150×0.045 in., Essex Corp.) was wrapped in 24 layers over a length of 44 cm, with fiberglass spacers between every pair of layers to allow the liquid nitrogen to contact all points of the coil. The adjacent layers were separated by Mylar film to prevent short circuits, and the magnet was oriented vertically to facilitate the flow of liquid as the nitrogen boiled away. Even at the highest fields used (6.2 kG), the heating of the magnet over the course of a scan was not severe (as measured by a 10% increase in resistance), but the liquid nitrogen boiled off at a rapid rate.

The magnetic field was homogeneous to 1% between the shim coils, which were constructed by wrapping ten additional layers, each 5.8 cm long, at both ends of the solenoid. Reproducibility of the magnetic field was tested to be 0.04% at room temperature (using fields below 1.5 kG), and 0.06% with liquid nitrogen cooling (fields up to 6.2 kG), although some error in the latter measurement could arise from temperature changes in the Hall probe (F.W. Bell No. 811A). The magnet power supply and feedback control unit are made by Walker Scientific, model FFC-4DP.

The discharge cell was constructed from Pyrex, with a 25 mm ID and a liquid nitrogen cooling jacket. Both the cathode (15.2 cm long) and the anode (3.7 cm long) were made from stainless steel tubing (16 mm ID, 3.5 mm wall), and placed entirely within the homogeneous field region of the solenoid magnet. A gas mixture containing Ar, H₂, and D₂ was flowed through the cell at a pressure of 10 mT, enabling spectra of both isotopomers to be recorded without altering the discharge conditions. The cell was pumped by a 6 in. diffusion pump. The negative glow discharge was operated with a discharge current of 5 mA. Higher currents yielded increased ion density, but produced more frequent transient voltage spikes which destroy the fragile diode contact in the Schottky mixer.

Using identical discharge pressures for both isotopomers was found to be extremely critical for precise *g*-factor determination, and is believed to be the source of disagreement between the current results and those previously reported. For example, during the course of one set of scans, the discharge pressure was inadvertently allowed to decrease by about 25%, although the actual pressure change within the cell is difficult to determine because of the pressure drop in the vacuum line. The ArH⁺ line profiles became noticeably asymmetric, with a finite absorption on the zero field side of both peaks. The line asymmetry was accompanied by a decrease in the splitting/magnetic field ratio of about 5%, as well as by increased scatter of the measured splittings. The line shape asymmetry was less noticeable for the ArD⁺ spectra, where the Zeeman components were not as fully resolved. The spectra which exhibited the distorted line profiles were not included in the present analysis.

This line shape asymmetry is consistent with the interpretation that the discharge extends beyond the electrodes at lower pressure, with a substantial fraction of the ions residing in the inhomogeneous region of a lower field outside the

shim coils. If such a drop in pressure occurred unnoticed during the first data set, for which separate gas mixtures were used, it would have caused a systematic error in the ratio of the ArH⁺ to ArD⁺ *g* factors. Because the magnetic fields used in the first experiment were lower, the line shape asymmetry would have been less apparent.

RESULTS

Error analysis

The results of the new *g*-factor measurements, including the equilibrium extrapolations discussed below, are shown in Table I. Absolute errors for the *g* factors are subject to calibration error and inhomogeneity of the magnetic field, and therefore would be on the order of 1%. The relative error between the two *g* factors is more significant for a dipole moment determination, because it contributes an uncertainty in the dipole moment much greater than 1%. Only the relative error is presented in Table I, which is determined exclusively from the scatter in the measurements which were made.

For systematic errors to cause a shift in the measured ratio of the *g* factors, they would have to survive the frequent alternation between ArH⁺ and ArD⁺ measurements. Otherwise, they would appear as a random error. For example, a gradual change in the magnetic field calibration which might occur due to thermal contraction of the solenoid would affect both ArH⁺ and ArD⁺ spectra similarly. Likewise, a change in the spatial location of the ions due to changing pressure or discharge current would influence both isotopomers equally.

The spectral baseline which is inherent in any frequency modulation scheme is unique to each isotopomer and causes a systematic error. A very crude estimate of the resulting shift in line center has been made for several of the scans collected. For recent data sets, the estimated shift was several kHz, or about a 0.1% change in *g_r*. Scans from the previous set (Ref. 1) had estimated shifts of about 10 kHz, corresponding to a 0.5% change in *g_r*. These shifts translate into an error in the dipole moment of 0.1 and 0.6 D, respectively. To some extent, the baseline shifts in peak position should appear as a random error, because the range of magnetic fields used in the experiment causes the peaks to be superimposed on different baseline patterns. Reduction of the baseline effects could be accomplished by increasing the magnetic field strength, or by improving the resolution or signal to

TABLE I. Rotational *g* factors and equilibrium extrapolations for ArH⁺ and ArD⁺.^a

Molecule	$g_r(v=0)$	g_r^{elec}	$g_r(R_e)$ (Gruebele <i>et al.</i>)	$g_r(R_e)$ ($l=4.74$)
ArH ⁺	0.6638(34)	−0.3228	0.6668	0.6791
ArD ⁺	0.3295(16)	−0.1686	0.3307	0.3354

^aEquilibrium *g* factors are obtained using either the method of Gruebele *et al.* (Ref. 8) or Ramsey (using a parameter $l=4.74$) (Ref. 12). The nuclear contributions to the *g* factors are $g_r^{\text{nuc}}(\text{ArH}^+) = 0.986\ 57$ and $g_r^{\text{nuc}}(\text{ArD}^+) = 0.498\ 156$, where $g_r = g_r^{\text{nuc}} + g_r^{\text{elec}}$. Error bars shown are relative, and do not include field calibration and baseline effects.

baseline ratio. A change in the splitting calculated by the fitting program due to the unresolved peaks would also cause a systematic error, because the ArD^+ g factor is approximately one half the ArH^+ g factor, and therefore was less well resolved for the fields used here. However, tests made at low magnetic fields indicated that the fitting of overlapping peaks is not a serious problem.

The most recent data sets give a value for $g_r(\text{ArH}^+) = 0.6638(34)$ and $g_r(\text{ArD}^+) = 0.3295(16)$, where the error (2σ) is a relative error, not including errors in calibration of the magnetic field. The ratio $g_r(\text{ArH}^+)/g_r(\text{ArD}^+) = 2.016(14)$, which disagrees substantially with the previous result of 1.973(19).¹ While the error bars given for g_r are only slightly lower for the new data set, we believe that these new results are less affected by systematic errors. The most likely systematic error affecting the previous result is the dependence of the plasma location on sample cell pressure. The previous data set was recorded using two different gas mixtures for the two isotopomers, while the current results were obtained with a single gas mixture containing both H_2 and D_2 .

Vibrational dependence of g_r

As discussed in Ref. 2, the different zero point vibrations of the two isotopomers can cause a significant error in the dipole moment calculation if not accounted for properly. Ideally, experimental extrapolation of the rotational g factors to yield equilibrium values could be made by observing vibrational satellites. Liu *et al.*⁹ were able to observe pure rotational spectra of vibrationally excited ArH^+ up to $v = 4$ in the infrared at $25 \mu\text{m}$ using a positive column plasma. Their discharge contained He, Ar, and H_2 at a current density of 0.13 A cm^{-2} , and could produce a population in $v = 1$ down in intensity from $v = 0$ by only a factor of 3. Unfortunately, the low pressure liquid nitrogen cooled negative glow discharge used for FIR spectroscopy (10 mT and 0.0015 A cm^{-2}) has been found to have a much lower vibrational temperature ($\sim 230 \text{ K}$ for HCO^+ ¹⁰), and we have had no success in observing the vibrational satellites.

In order to extrapolate the g factors to obtain equilibrium values, an analogy was previously made to the neutral molecule HF, for which the vibrational dependence has been experimentally determined.¹¹ In treating the dependence of g_r on bond length, the matrix element summation which occurs in the electronic contribution to g_r ,

$$S = \sum_{n \neq 0} \frac{|\langle n | L_x | 0 \rangle|^2}{E_n - E_0} \quad (2)$$

which has an identical value for a given bond length for both isotopomers, was assumed to vary as $(R/R_e)^l$, where l is an empirically determined parameter.¹² The experimental g factors for HF $v = 0$ and $v = 1$ give $l = 4.74$, and this value for the parameter l was used to estimate equilibrium g factors for ArH^+ and ArD^+ as well.

Recently, another method has been devised to extrapolate the rotational g factors to their equilibrium values. Gruebele *et al.*¹³ have fit the Zeeman, rotational, and rovibrational spectra of ArH^+ and ArD^+ to obtain a molecular potential function. Because the g factor describes the elec-

tronic motion in the rotating molecule, a change in the g factor upon stretching the bond should influence the rotational energy level spacing of highly excited vibrational levels. Although the effect is small, they determined the parameter for the vibrational dependence of g_r in the case of ArH^+ and ArD^+ (for which rovibrational spectra up to $v = 7$ and $v = 4$, respectively, were available^{14,15}). Their results yielded the formula $g_r(v) = g_r^{\text{eq}} + \alpha(v + 1/2)$, where $\alpha = -0.0059$ for ArH^+ and -0.0021 for ArD^+ .

While the method of fitting rovibrational energy levels barely determines the vibrational dependence of g_r due to correlation among the molecular constants, it is more satisfactory from a theoretical perspective. Although ArH^+ is similar in bond strength and bond length to the isovalent neutral molecule HF, at bond lengths near dissociation the dependence of g_r on R is qualitatively different. For neutral molecules, $g_r \rightarrow 0$ as R becomes very large, whereas for molecular ions g_r remains finite (and large in the case of ArH^+) because of the net charge on one of the atoms.

DISCUSSION

The dipole moment of ArH^+ calculated from the rotational g factors measured in this work is presented in Table II. As can be seen, the difference between the g -factor results is accentuated in the dipole moment calculation because the ratio g_r/B is nearly equal for the two isotopomers. For comparison, the dipole is calculated from (a) ground vibrational state g factors, (b) extrapolated equilibrium g factors using the method of Gruebele *et al.*,¹³ and (c) extrapolated equilibrium g factors based on the analogy with HF using $l = 4.74$. Method (b) is considered to yield the most satisfactory value, $\mu = 3.0(6) \text{ D}$ (2σ error).

A high quality *ab initio* calculation by Rosmus⁶ using the CEPA (coupled electron pair approximation) method yielded a dipole moment of 2.2 D , with an estimated uncertainty of about 0.1 D . Pyykko *et al.*¹⁶ have performed a numerical Hartree-Fock calculation, from which they concluded that basis set limitations do not generate a substantial error in Rosmus' calculation. The current experimental results are still slightly outside of the 2σ error range of the theoretical value. However, the vibrational correction to the g factors still presents an uncertainty due to the lack of ex-

TABLE II. Dipole moment of ArH^+ (Debye).^a

Unextrapolated	Extrapolated (Gruebele <i>et al.</i>)	Extrapolated ($l = 4.74$)
2.84(59)	2.95	3.35

^a Calculations for the dipole moment of ArH^+ with respect to the center of mass from rotational g factors using (1) unextrapolated vibrational ground state g factors; and equilibrium g factors extrapolated using either the method of (2) Gruebele *et al.* (Ref. 8) or (3) Ramsey (Ref. 12) (using a parameter $l = 4.74$). The dipole moment of ArD^+ can be found by $\mu(\text{ArH}^+) = \mu(\text{ArD}^+) + 0.14 \text{ D}$ which results from the center of mass shift. Error bars quoted are 2σ , and represent the error in the ground state g factors only, with additional errors arising from baseline effects and the extrapolation method. An *ab initio* theoretical value of 2.2 D for $v = 0$ is predicted by Rosmus (Ref. 20).

perimental data in excited vibrational states.

In order to make a useful comparison with *ab initio* theory, two advances must be made: First, the *g*-factor measurements should be made at substantially higher fields, requiring a superconducting magnet, in order to reduce the experimental error. Second, for the case of ArH^+ , experimental data for excited vibrational states must be obtained. Fortunately, with many other interesting molecular ions, the extrapolation of the rotational *g* factors to an equilibrium value is not crucial because an isotopic substitution can be made without substantially altering the zero point vibrations of the molecule. For example, HCO^+ can be studied using the isotopomeric pair $\text{H}^{13}\text{CO}^+/\text{HC}^{18}\text{O}^+$, yielding a ground state dipole moment with no need to extrapolate the rotational *g* factors.

In light of these studies, the best route to the determination of molecular ion dipole moments appears to be the present method, but substantially improved precision in the measurement of rotational *g* factors will be required for genuinely useful results. This can probably be best achieved by using millimeter–submillimeter spectroscopy, with the corresponding linewidth reduction and increased frequency accuracy. We expect that such results will become available in the near future.

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