Determination of the Dipole Moment of ArH $^+$ from the Rotational Zeeman Effect by Tunable Far-Infrared Laser Spectroscopy

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The first determination of the electric dipole moment of a molecular ion is reported. A tunable far-infrared laser was used to measure the Zeeman effect in low-J rotational transitions of ArH $^+$ and ArD $^+$, and the dipole moment was determined from the isotopic dependence of g_r. The result ($\mu = 1.4 \pm 0.4$ D) is in marginal agreement with *ab initio* calculations (2.2 D). It is shown that this method can ultimately provide molecular-ion dipole moments accurate to within a few percent. The adiabatic internuclear separations of both isotopes were also determined from the g_r values.

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The permanent electric dipole moment of a molecule is an important property for the characterization of its electronic structure and radiative–energy-transfer processes. For neutral molecules, precise measurements ($\sim 0.01\%$) of dipole moments have been carried out exclusively through use of the Stark effect. Because charged molecules are accelerated in an electric field, observation of the Stark effect becomes impractical, and an experimental determination of the electric dipole of an ion has not yet been made. As shown by Townes *et al.*,[1-3] measurement of the rotational g factor (g_r) for two isotopes of a linear molecule allows the determination of both the magnitude and sign of the electric dipole. Such a determination of the dipole moment from the Zeeman effect is intrinsically less accurate because the dipole moment is proportional to the small difference between g_r/B for two isotopes, where B is the rotational constant. However, it provides a direct experimental route to a quantity previously unavailable for molecular ions.

Knowledge of the rotational g factor is also required for calculation of the equilibrium internuclear separation of a diatomic molecule, with the bond length directly amenable to *ab initio* calculations. As shown by Gordy and Cook,[3] g_r is used to calculate the contribution of electronic motion to the molecular moment of inertia, an effect which is easily observed by high-resolution spectroscopy. With the use of accurate Dunham coefficients from vibrational spectra, the formalism developed by Watson[4] provides a means of our separately determining the adiabatic potential minima for each isotope, and quantitatively evaluating the breakdown of the Born-Oppenheimer approximation.

In the present study, we have used a tunable far-infrared laser to measure the $J = 1 \leftarrow 0$ transition of ArH $^+$ and the $J = 2 \leftarrow 1$ transition of ArD $^+$. The ions were generated in a glow discharge, and magnetic fields up to 4 kG were used to measure rotational g factors. The current experiment permitted only a rough determination of the dipole moment of ArH $^+$. However, it is shown that the method could be improved, making possible the measurement of molecular-ion dipole moments with a precision of a few percent.

The tunable far-infrared laser spectrometer is similar in design to others described previously.[5-7] A far-infrared (FIR) laser (1.5 m long, 38 mm bore), optically pumped by a CO $_2$ laser (1.2 m long, 6.75 mm bore, 40 W output), provides line-tunable radiation of ~ 1 mW power at frequencies ranging from 600 to 4000 GHz. The output is mixed with a microwave source (Hewlett-Packard model 8673B with 8349B amplifier, 100 mW from 2 to 20 GHz) by means of a GaAs Schottky-barrier diode (Robert J. Mattauch of the University of Virginia, Charlottesville, VA; No. 1E7) mounted in an open-structure corner cube.[8] The continuously tunable sideband power of ~ 1 μW is separated from the laser carrier by a Michelson diplexer,[9] and passed through the cell to a liquid-helium–cooled InSb bolometer (Cochise Instruments). The spectra were taken with use of tone-burst modulation of the microwave source,[10] and digitally recorded with a PDP-11/23 computer.

A magnetically confined extended negative glow discharge[11] was used to produce the ArH $^+$ and ArD $^+$ ions. The 65-cm-long×10-cm-i.d. solenoid was wound with five layers of 10-gauge magnet wire, shimmed at both ends with two additional layers 5 cm long, and liquid-nitrogen cooled. Both the cathode and the anode were located entirely between the shim coils, where the measured axial field was homogeneous to 1.6%. The magnet power supply was stabilized by a feedback circuit from a rotating-coil magnetic field probe (Walker model FFC-4DP), resulting in fields reproducible to 0.01%. A magnetic field calibration was performed before and after the g-factor measurements by the use of a Hall-effect gaussmeter (F.W. Bell Inc., model 811A). The field calibrations agreed to within 0.15%. Uncertainties in the magnetic field made a negligible contribution to the error in the dipole moment.

A 60:1 mixture of Ar and H $_2$ optimized the ArH $^+$ absorption at a pressure of 20 mT, a discharge current of
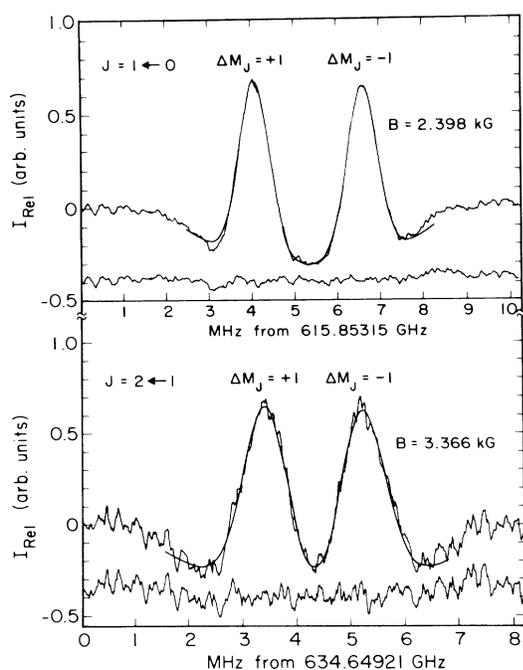
FIG. 1. Rotational spectra of ArH$^+$ (top) and ArD$^+$ (bottom) showing the magnetic splitting. The fitted lines are superimposed on the observed spectrum, and the residuals are shown below.

FIG. 2. Rotational Zeeman-effect splitting vs magnetic field for ArH$^+$ and ArD$^+$.

12 mA, and liquid-nitrogen cooling of the cell. As found by Bowman et al.,[12] H$_2$ pressures of ~1 mT or more greatly reduced the absorption. The ArH$^+$ absorption was strongest at about 500 G and decreased somewhat, but not dramatically, at fields up to 4 kG.

Both the ArH$^+$ $J=1 \leftarrow 0$ and the ArD$^+$ $J=2 \leftarrow 1$ transitions were measured by use of the 496-μm (604-GHz) CH$_3$F laser line. For determination of the magnetic splittings, scans were taken at various magnetic fields ranging from 800 to 4000 G. Because the magnetic field from the solenoid is perpendicular to the electric field of the FIR radiation, only $\Delta M_J = \pm 1$ transitions are observed. Each spectrum was fitted by a sum of two second-derivative Lorentzian line shapes, which proved superior to a second-derivative Gaussian, presumably because of the modulation scheme. Scans for ArH$^+$ and ArD$^+$ are shown in Fig. 1, and the g factors from the accumulated data are given in Fig. 2.

The method for the calculation of the electric dipole moment from rotational g factors was first derived by Townes et al.[1] A more general formula, valid for ions, is given by Townes and Schawlow[2]:

$$\mu = (he/8\pi^2 M_p \Delta z)(g_r'/B_e' - g_r/B_e) - \tfrac{1}{2} Qe \Delta z, \qquad (1)$$

where μ is the electric dipole moment, B_e is the equilibrium rotational constant (in hertz), g_r is the rotational g factor, Δz is the displacement of center of mass with isotopic substitution, Qe is the charge of the ion, and M_p is the proton mass. The last term reflects the fact that the dipole moment is different for two isotopes of an ion, and follows from the original derivation[1] if second-order terms are retained.

To assess the accuracy of the above equation for determination of μ, other magnetic interactions in the molecule must be considered. The magnetic susceptibility anisotropy, $\chi_\parallel - \chi_\perp$, shifts the energy levels of HCl by only ~800 Hz at 4 kG,[13] and because of the M^2 dependence of the perturbation it has no effect on the measured splitting. The nuclear Zeeman effect also does not affect the splittings. The proton nuclear spin-rotation coupling is 42 kHz for HCl, so that $\Delta M_I \neq 0$ transitions are very weakly allowed, and the shielding effect for the proton at 4 kG is less than 100 Hz.[14]

The largest error in the model would be caused by the vibrational-state dependence of g_r. The theory used to derive the formula for μ assumes that the structural properties of the molecule remain constant when an isotopic substitution is made, and therefore the equilibrium g_r and B values should be used. While it is shown below that zero-point vibration causes only a 1.5% change in g_r for ArH$^+$, the dipole moment is significantly affected because $g_r'/B_e' \approx g_r/B_e$. g_r can be written as a sum of nuclear and electronic contributions, where the nuclear term is independent of R (Ref. 3):

$$g_r = [M_p/(M_1 + M_2)](Z_1 M_2/M_1 + Z_2 M_1/M_2) - (2M_p/m_e I) \sum_{n \neq 0} |\langle 0 | L_x | n \rangle|^2/(E_n - E_0). \qquad (2)$$

In order to extrapolate g_r to its equilibrium value, Ramsey has proposed that the summation in the electronic term above be approximated as R^l, where l is an empirical constant.[15] The electronic contribution to g_r is then proportional to R^{l-2}. Expanding g_r^{elec} about R_e and evaluating $\langle \xi \rangle$ and $\langle \xi^2 \rangle$ [$\xi = (R - R_e)/R_e$] in terms of the potential constant a_1
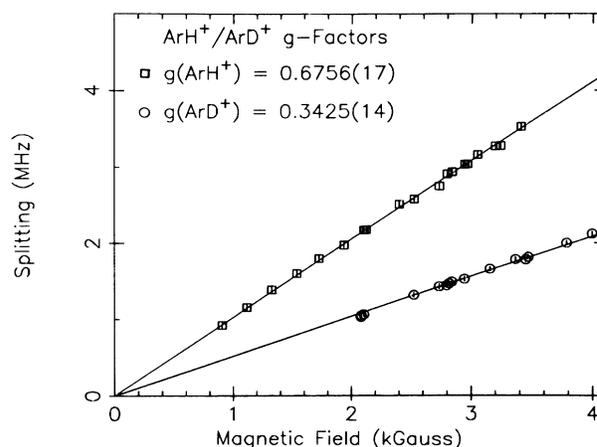
TABLE I. Rotational g factors and dipole moments for ArH^+ and HF, H_2, and LiH. μ is the dipole moment calculated from the equilibrium values g_r^{eq}, and $\mu(g_r^{eq}) = \mu(g_r) + \Delta\mu$. μ_0(Stark) is the dipole moment for $v = 0$ obtained by measurement of the Stark effect.

Molecule	g_r	g_r^{eq}	μ	$\Delta\mu$	μ_0(Stark)	Reference g_r	μ_0
ArH^+	0.6756(17)[a]	0.6860[b]	1.42(40)[a]	0.38[b]	· · ·		
ArD^+	0.3425(14)[a]	0.3463[b]	1.28(40)[a]	0.38[b]	· · ·		
HF	0.74104(15)	0.75017[b]	1.87(44)	0.07[b]	1.826526(7)	13	19
DF	0.369(5)	0.373[b]				20	
H_2	0.88291(7)	0.89668[c]	−0.051(2)	−0.053[c]	0	21	
HD	0.663211(14)	0.680511[c]				16	
LiH	−0.654(7)	d	−5.90(40)	d	5.882(3)	22	23
LiD	−0.272(5)	d				22	

[a]Error bars here are 1σ.
[b]g_r has been extrapolated using $l = 4$ to give the equilibrium value g_r^{eq}.
[c]g_r has been extrapolated using $l = 3.7$.
[d]Because of the radically different electronic distribution of LiH, no such extrapolation was made.

gives[13]

$$\langle g_r^{elec}\rangle_{v,J} = g_r^{elec}(R_e)\{1 + (B_e/\omega_e)(v + \tfrac{1}{2})[(l-2)(-3a_1) + (l-2)(l-3)] + O((B_e/\omega_e)^2)\}. \tag{3}$$

Quinn et al. were able to correlate their beam measurements for H_2, HD, and D_2 to 0.01% accuracy with this formula, finding $l = 3.7$.[16] The same value of l was obtained by use of the variation in R due to zero-point vibrations and centrifugal distortion.

The dependence of g_r on R for ArH^+ could be tested if there was sufficient sensitivity to observe the vibrational satellites, and a reasonable estimate could be made by observation of this effect in the isoelectronic neutral species, HCl. Unfortunately no such data exist, but a theoretical calculation for HF gives $l = 4.3$.[17] If we take $l = 4$ as a reasonable value and use $a_1 = -0.2564$,[3,18] then $\Delta g^{elec}/g^{elec} = 3.4\%$ for ArH^+ and 2.4% for ArD^+. This translates into a dipole moment higher by 0.38 D than what is obtained from uncorrected g_r's. If l is allowed to vary between $3 < l < 5$, then the dipole correction varies between $0.19 \text{ D} < \Delta\mu < 0.57$ D. Future work to measure ion dipole moments more accurately would require an experimental investigation of vibrational effects.

The rotational g factors and dipole moments are presented in Table I. To provide an experimental test of the method, calculations based on the literature data for HF, LiH, and H_2 are included, and these are compared with accurate Stark values. The result for ArH^+ (corrected for vibrations), $\mu = 1.4 \pm 0.4$ D (1σ), lies just within the 2σ range of the theoretical value of 2.2 D, calculated by Rosmus by use of the coupled–electron-pair–approximation (CEPA) method.[24]

The uncertainty in g_r could be improved both by our increasing the magnetic field and by stabilizing the FIR-laser. A magnet capable of 30 kG, for example, would reduce the error in g_r by a factor of 8. The contribution to the error in the dipole moment of ArH^+ would then be only 0.05 D (1σ). FIR laser frequency stability was also a source of error in the determination of g_r. Although the error in the splitting for a single scan was 5 kHz, the rms deviation of the splitting versus field was 25 kHz. If the FIR laser could be stabilized to <5 kHz for the duration of a single scan, then the line fit should improve to this level of accuracy. With corrections for zero-point vibrations, dipole moments determined by this technique should ultimately be accurate to a few percent.

To calculate the equilibrium internuclear separation of ArH^+ and ArD^+, we have combined the Dunham coefficients from the work of Brault and Davis,[25] Bowman et al.,[12] and Johns[18] with the rotational g factors presented here. Watson[4] has shown that the Dunham coefficient Y_{01} is related to the adiabatic potential minimum r_e^{ad} by

$$Y_{01} = \frac{h}{8\pi^2\mu_{atoms}(r_e^{ad})^2}\left[1 + \frac{\Delta Y_{01}^{(D)}}{B_e} + \frac{m_e}{M_p}g_r\right], \tag{4}$$

where μ_{atoms} is the reduced mass of the atoms, $\Delta Y_{01}^{(D)}$ is the Dunham correction to Y_{01}, and g_r is the rotational g factor (in nuclear magnetons). He has also shown that the Born-Oppenheimer potential minimum r_e^{BO} can be extracted by measurement r_e^{ad} for different isotopes:

$$r_e^{ad} = r_e^{BO}[1 + m_e(d_H/M_H + d_{Ar}/M_{Ar})], \tag{5}$$

where d_H and d_{Ar} are isotopically invariant parameters. Although only the hydrogen was isotopically substituted, the above equation can still be applied with some accuracy by neglect of d_{Ar}. Because $M_{Ar} \gg M_H$, d_{Ar}/M_{Ar} is much less important than d_H/M_H [for HCl, $d_H = 0.155(15)$ and $d_{Cl} = 0.116(46)$],[4] and neglect of d_{Ar} should only introduce an error of several percent.

A summary of the corrections to r_e is presented in

TABLE II. Equilibrium internuclear separations for ArH^+ and ArD^+. r_e^{ad} is calculated after application of the Dunham and rotational g-factor corrections [see Eq. (4)]. r_e^{BO} is the Born-Oppenheimer potential minimum derived from Eq. (5). $d_H = 0.268(10)$ [from Eq. (5)]. Y_{01} and $\Delta Y_0^{(p)}$ (see Ref. 18). $BI = 505.37905$ GHz $Å^2/u$ (see Ref. 26).

Molecule	r_e^{ad}	r_e^{BO}	r_e^{BO} (theory)[a]
ArH^+	1.280561(2)	1.280375(7)	1.286
ArD^+	1.280468(2)		

[a]The theoretical value is from Ref. 24.

Table II. The inclusion of g_r in the calculation of the equilibrium bond length changes r_e by 0.00023 Å. Rosmus's CEPA calculation yielded a value for r_e^{BO} which was 0.006 Å higher than the experimental result.[24]

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