Determination of the Dipole Moments of Molecular Ions from the Rotational Zeeman Effect by Tunable Far-Infrared Laser Spectroscopy [and Discussion]

K. B. Laughlin, G. A. Blake, R. C. Cohen, D. C. Hovde, R. J. Saykally, H.-J. Foth, E. Hirota and T. Oka

Phil. Trans. R. Soc. Lond. A 1988 **324**, 109-119
doi: 10.1098/rsta.1988.0004

Phil. Trans. R. Soc. Lond. A **234**, 109–119 (1988)
Printed in Great Britain

Determination of the dipole moments of molecular ions from the rotational Zeeman effect by tunable far-infrared laser spectroscopy

By K. B. Laughlin, G. A. Blake, R. C. Cohen, D. C. Hovde and R. J. Saykally
Department of Chemistry, University of California, Berkeley, California 94720, *U.S.A.*

The details of the first experimental determination of the dipole moment of a molecular ion from the rotational Zeeman effect are presented, along with an assessment of the ultimate accuracy of the technique.

The permanent electric-dipole moment of a molecule is an important property for characterizing its electronic structure and radiative energy-transfer processes. For a large number of neutral molecules, precise measurements (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 experimental determination of the electric dipole of an ion has not yet been made, although the dipole derivative of CH_2^- has been determined by Okumura *et al.* (1987) from measurements of the radiative lifetimes of its excited vibrational states. As shown by Townes & Schawlow (1955), Townes *et al.* (1975) and Gordy & Cook (1970), measurement of the rotational g-factors (g_r) for two isotopes of a linear molecule allows the determination of both the magnitude and sign of the electric dipole. For asymmetric molecules, the isotopic dependence of the full g-tensor must be evaluated. 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. There are also systematic errors associated with the zero-point vibrations of the molecule if the dipole is calculated from ground-state g-factors instead of from equilibrium values. However, it provides a direct experimental route to a quantity previously unavailable for molecular ions.

In the present study, we have used a tunable far-infrared (FIR) 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^+. It is shown that the method could be improved, making possible the measurement of molecular ion dipole moments with a precision of about 0.1 D‡.

The magnetic effects described in detail below are most prominent in hydrogenic molecules, for which rotational transitions occur predominantly in the submillimetre and FIR regions of the electromagnetic spectrum. The induced field splittings are quite small, on the order of one part in 10^5, and a spectrometer designed to measure these effects must overcome not only the technological difficulties of spectroscopic work in the FIR, but must also possess the sensitivity, resolution, and stability to analyse such small perturbations of the rotational spectra of reactive

† $1\ G = 10^{-4}\ T$.
‡ $1\ D = 3.33 \times 10^{-30}\ C\ m$.

ions with high precision. The tunable FIR spectrometer we have constructed for this purpose at Berkeley has been used to study a number of reactive intermediates in the FIR, and is similar in design to others described previously (Bicanic *et al.* 1978; Fetterman *et al.* 1978; Farhoomand *et al.* 1985). A schematic outline of the spectrometer is presented in figure 1.

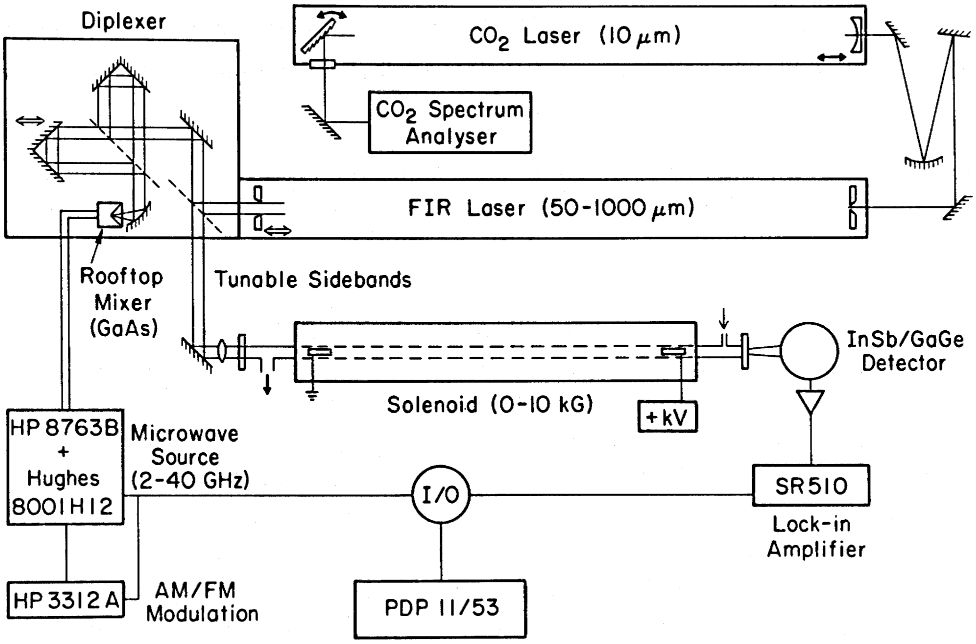

FIGURE 1. Schematic diagram of tunable far-infrared laser spectrometer.

Briefly, by mixing radiation from a fixed-frequency, optically pumped molecular gas laser with that from a tunable microwave oscillator, the resolution and accuracy traditionally associated with conventional microwave spectrometers is upconverted into the FIR were absorption strengths of most molecules are considerably greater. In the initial version of the spectrometer, an 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), provided line-tunable radiation of 1–10 mW between 600 and 4000 GHz. A more recent modification of the spectrometer incorporates a commercial 150 W CO_2 laser (Apollo no. 150) and an enlarged FIR cavity (2.3 m, 38 mm bore), which produces line-tunable radiation in the same range, but at greater power levels (50–1000 mW). The microwave radiation that is mixed with the laser is produced by a Hewlett–Packard model 8673B source (2–26.5 GHz) along with a Spacek Ka-2X frequency doubler and a Hughes 8001H12 travelling wave tube amplifier to provide continuous sideband coverage between 2–40 GHz.

A GaAs Schottky-barrier diode (obtained from R. J. Mattauch, University of Virgina) is used to mix the laser and microwave components. The open-structure rooftop mixer in which it is housed is designed to be as broadband as possible at both FIR and microwave frequencies to increase the operational bandwidth of the spectrometer. By sloping the ground plane of the mixer device and contacting the diode with a AuNi long-wire antenna mounted in front of a tunable rooftop reflector (Betz & Zmuidzinas 1984) whose whisper–apex separation may be varied between 100–1000 μm, the FIR optical coupling efficiency is kept nearly constant over a two octave range without creating an efficient retroflector for the laser. The whisker mount mimics a 50 Ω transmission line except for a short (2 mm) length of wire that gives some flexibility to the antenna. Sufficient microwave radiation can be coupled coaxially up to 23.5 GHz with as little as 10 mW of power. With improved microwave components, coaxial coupling could be extended to much higher frequencies. Frequencies above 26 GHz are coupled onto the diode via a WR-28 waveguide placed in the body of the mixer. Spectra are taken by using either $2f$ sine wave or tone-burst frequency modulation (Pickett 1977) of the microwave source, and are digitally recorded with a PDP-11/53 computer.

The laser radiation is coupled onto the diode after passing through a Martin–Puplett polarization interferometer, which has the advantage of coupling arbitrary laser polarizations onto the diode while simultaneously filtering out the tunable sidebands whose polarization is rotated 90° with respect to the laser (Martin & Puplett 1969). A tunable metal mesh Fabry–Perot cavity between the output of the interferometer and the detector increases the filtering of the much more intense laser carrier. Another Fabry–Perot between the laser and corner cube reduces large baselines associated with leaked sideband power being absorbed by sharp resonances with the FIR laser cavity. With the new system, sideband power levels between 100–200 μW have been measured in the 20–30 cm^{-1} region.

A magnetically confined extended negative glow DC discharge was used to produce the ArH^+ and ArD^+ ions (DeLucia *et al.* 1983). With this cell, ion densities as high as 5×10^{12} cm^{-3} have been measured for HCO^+ at a total pressure of 50 mTorr. Our experiments were performed with a 65 cm long × 10 cm internal diameter solenoid wound with five layers of 10 gauge magnet wire, shimmed at both ends with two additional layers 5 cm long, and cooled by liquid nitrogen. The maximum usable field was about 4 kG, limited mainly by the cooling efficiency of the magnet and jacket design. Both the cathode and the anode were located entirely between the shim coils, where the measured axial field was homogenous to 1.6 %. The magnet power supply was stabilized by a feedback circuit from a rotating coil 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 mTorr, a discharge current of 12 mA, and with liquid nitrogen cooling of the cell. As found by Bowman *et al.* (1983), H_2 pressures of *ca.* 1 mTorr 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 using the 496 μm (604 GHz) CH_3F laser line. For determination of the magnetic splittings, scans were taken over a range of magnetic fields from 800 to 4000 G. Because the magnetic field from the solenoid is perpendicular to the electric field of the FIR radiation, only $\Delta M = \pm 1$ 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 figure 2, and the g-factors from the accumulated data are given in figure 3.

To assess the accuracy of the above data for determination of the rotational g-factors, other magnetic interactions in the molecule must be considered. The magnetic susceptibility anisotropy, $\chi_\parallel - \chi_\perp$, shifts the energy levels of the isoelectronic neutral molecule HCl by only 800 Hz at 4 kG (de Leeuw & Dymanus 1973), and because of the M^2 dependence of the

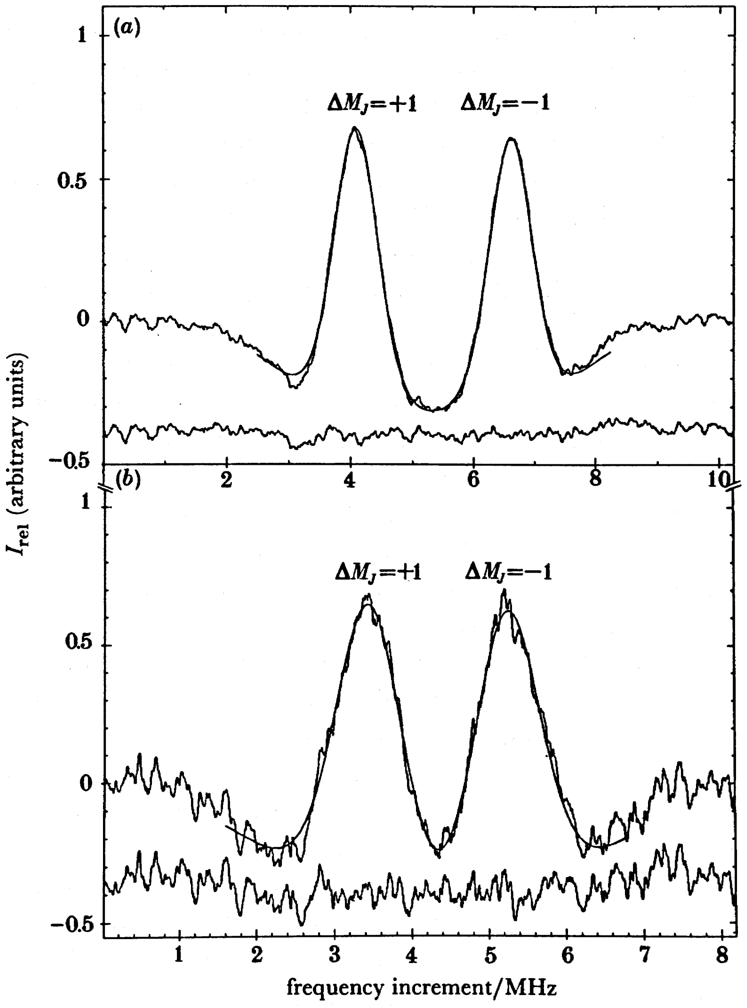

FIGURE 2. Rotational spectra for ArH^+ and ArD^+ showing the magnetic splitting. The fitted lines are superimposed on the observed spectrum, and the residuals are shown below. (*a*) ArH^+, $J = 1 \leftarrow 0$, frequency from 615.853 15 GHz, B = 2.398 G; (*b*) ArD^+, $J = 2 \leftarrow 1$, frequency from 634.649 21 GHz, B = 3.366 KG.

perturbation it has no effect on the measured splittings. The proton nuclear spin–rotation coupling is 42 kHz for HCl, so that $\Delta M_{\mathrm{I}} \neq 0$ transitions are only very weakly allowed, and the shielding effect for the proton at 4 kG is less than 100 Hz (Kaiser 1970). Therefore the measured splittings should be purely a function of the rotational *g*-factor, and are given by $\Delta\nu = 2H\beta_{\mathrm{I}}g_{\mathrm{r}}$, where H = magnetic field and β_{I} = nuclear magneton (in megahertz per gauss).

The method for calculating the electric dipole from rotational *g*-factors was first derived by Townes *et al.* (1955). The following is a short summary of the derivation presented in Gordy & Cook (1970). The rotational *g*-factor results from the end-over-end rotation of a molecule with imbalanced nuclear and electronic charge. We can express g_{r} as a sum of nuclear and electronic contributions:

$$\left.\begin{aligned} g_{xx} &= \frac{M_{\mathrm{p}}}{I_x}\sum_k Z_k(y_k^2+z_k^2) - \frac{2M_{\mathrm{p}}}{mI_x}\sum_{n\neq 0}\frac{|\langle n|L_x|0\rangle|^2}{E_n-E_0} \\ &= g_{xx}^{\mathrm{nuc}} + g_{xx}^{\mathrm{el}}, \end{aligned}\right\} \qquad (1)$$

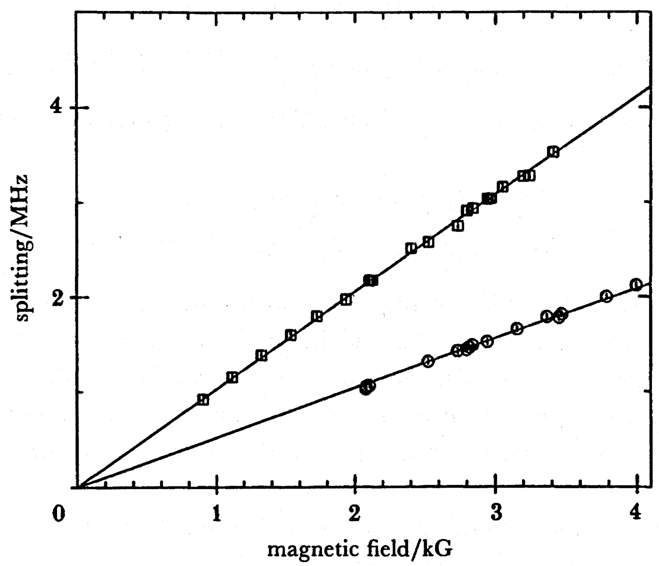

Figure 3. Rotational Zeeman-effect splitting against magnetic field for ArH⁺ and ArH⁺. Symbols: □, $g_r(\text{ArH}^+) = 0.675\,6(17)$; ○, $g_r(\text{ArD}^+) = 0.342\,5(14)$.

where M_p = mass of the proton, I_x = moment of inertia of the molecule about the x axis, Z_k = charge of nucleus k, y_k and a_k = coordinates of nucleus k, m = mass of the electron, L_x = electronic angular momentum about the x axis, E_n, E_0 = energy of electronically excited state n and ground state 0.

The formula for the magnetic susceptibility

$$\chi_{xx} = \frac{-e^2}{4mc^2}\langle 0|\sum_i y_i^2 + z_i^2|0\rangle + \frac{e^2}{2m^2c^2}\sum_{n\neq 0}\frac{|\langle n|L_x|0\rangle|^2}{E_n - E_0}, \tag{2}$$

where y_i, z_i = coordinates of electron i, can be substituted into (1), giving:

$$I_x g_{xx} = M_p[\sum_k Z_k(y_k^2 + z_k^2) - \sum_i \langle 0|y_i^2 + z_i^2|0\rangle] - \frac{4mc^2}{e^2} M_p \chi_{xx}. \tag{3}$$

Assuming that an isotopic substitution is made that shifts the origin by (Δx, Δy, Δz) without affecting the structure of the molecule, (3) for the new isotope becomes

$$\begin{aligned} I'_x g'_{xx} = M_p[&\sum_k Z_k(y_k^2 - 2y_k\Delta y + \Delta y^2 + z_k^2 - 2z_k\Delta z + \Delta z^2) \\ &- \sum_i \langle 0|y_i^2 - 2y_i\Delta y + \Delta y^2 + z_i^2 - 2z_i\Delta z + \Delta z^2|0\rangle] - \frac{4mc^2}{e^2} M_p \chi'_{xx}. \end{aligned} \tag{4}$$

Van Vleck (1932) has shown that the magnetic susceptibility, χ_{xx}, is independent of the origin used. If the principal magnetic axes retain their orientation with respect to the principal inertial axes upon substitution, then $\chi_{xx} = \chi'_{xx}$. Subtracting (3) from (4) gives

$$I'_x g'_{xx} - I_x g_{xx} = -2M_p[\sum_k Z_k(y_k\Delta y + z_k\Delta z) - \sum_i \langle 0|y_i\Delta y + z_i\Delta z|0\rangle - \tfrac{1}{2}Q(\Delta y^2 + \Delta z^2)], \tag{5}$$

where Q is the net charge on the molecule. Rearranging (5) gives

$$I'_x g'_{xx} - I_x g_{xx} = (-2M_\mathrm{p}/e)[\mu_y \Delta y + \mu_z \Delta z - \tfrac{1}{2}(Qe)(\Delta y^2 + \Delta z^2)], \tag{6}$$

where μ_y, μ_z are components of the electric dipole. For a linear molecule, where $\Delta y = 0$ and $g_{xx} = g_{yy} = g_\mathrm{r}$,

$$\begin{aligned}\mu &= -(e/2M_\mathrm{p}\Delta z)(I'g' - Ig) + \tfrac{1}{2}(Qe\,\Delta z)\\ &= -(eh/16\pi^2 M_\mathrm{p}\Delta z)[(g'/B') - (g/B)] + \tfrac{1}{2}(Qe\,\Delta z),\end{aligned} \tag{7}$$

where B is the rotational constant. The assumption that the structure of the molecule remains constant upon isotopic substitution would hold if the nuclei were held at a fixed bond length. Because the zero-point vibrations alter the electronic structure, the g_r and B values used in (6) or (7) must rigorously be the equilibrium values (or the values at some other common point). The limit on the accuracy in this case would arise from the order of perturbation theory used in describing g_r and χ.

If g_r could be measured for more than one vibrational state, then an extrapolation could be made to the equilibrium geometry. The summation in (1),

$$S = \sum_{n\neq 0} \frac{|\langle n|L_x|0\rangle|^2}{E_n - E_0}, \tag{8}$$

is purely a function of the electronic structure, and has the same dependence on bond length for both isotopes if evaluated with the origin at the centroid of the electron distribution. To treat the variation of g_r with the bond length R, Ramsey (1952) assumed the summation S is proportional to $(R/R_\mathrm{e})^l$, where l is an empirical constant. A functional dependence of this type produces the correct behaviour of g_r as $R \rightarrow 0$, for $l > 2$. Quinn *et al.* (1958) were able to correlate their molecular beam measurements of g_r for H_2, HD, and D_2 from this equation, finding $l = 3.7$. The variation of g_r with vibrational state has been measured for SiO, Geo (Davis & Muenter 1974; Honerjager & Tischer 1973) and recently for HF (Bass *et al.* 1987). SiO and GeO show a very small dependence of g^el on v (0.13% and 0.12% respectively for $v = 0$ to $v = 1$). HF, on the other hand, shows a large dependence (11% for $v = 0$ to $v = 1$), two orders of magnitude higher than for SiO and GeO.

Because of the lack of data, the vibrational correction for ArH^+ is difficult to estimate. Structurally, ArH^+ is more similar to HF than to SiO, and the vibrational dependence of g^el should be closer to that for HF. If the summation S in (8) is proportional to R^l, then

$$\langle g^\mathrm{el}\rangle_{v,J} = g^{el}(R_e)\{1 + (B_\mathrm{e}/\omega_\mathrm{e})(v+\tfrac{1}{2})[-3a_1(l-2) + (l-2)(l-3)] + O(B_\mathrm{e}/\omega_\mathrm{e})^2)\}. \tag{9}$$

It is important to note that g^el in the above equation must be evaluated at the centroid of the electron distribution. However, only for HD (Quinn *et al.* 1958) and LiH/LiD (Lawrence *et al.* 1963) are the contributions to g^el due to a displacement of the electronic centroid from the centre of mass more than a few percent of the total g^el. For most molecules, taking g^el to be evaluated at the centre of mass when using (9) to extrapolate back to g^el (R_e) introduces negligible error. The g-factors for HF, $v = 0$ and $v = 1$ give $l = 4.74$. With this l value, the linear correction term accounts for 80% of the total correction. If we use this parameter to extrapolate g_r to give $g_\mathrm{r}(R_\mathrm{e})$, the dipole moments and corrections due to the extrapolation are given in table 1. To provide an experimental test of the method, calculations based on the literature data for HF, H_2, LiH, CO and GeO are included, and these are compared with the

TABLE 1. ROTATIONAL g-FACTORS AND DIPOLE MOMENTS FOR ArH^+ AND HF, H_2, LiH, CO AND GeO

(μ is the dipole moment calculated from $g_r(R_e)$, and $\mu = \mu(g_r(R_0)) + \Delta\mu$. μ_0 (Stark) is the experimental value for $v = 0$ obtained from the Stark effect.)

molecule	g_r	$g_r(R_e)$	μ	Δμ	μ_0(Stark)	references
ArH^+	0.6756 (17)[a]	0.6904[b]	1.59 (40)[a]	0.55	—	—
ArD^+	0.3425 (14)[a]	0.3479[b]	1.45 (40)[a]	—	—	—
HF	0.74104 (15)	0.75400[b]	1.93 (44)	0.13	1.826526 (7)	1, 2
DF	0.369 (5)	0.374[b]	—	—	—	3
LiH	−0.654 (7)	—	5.90 (40)	—	5.882 (3)	4, 5
LiD	−0.272 (5)	—	—	—	—	4
^{70}GeO	−0.141 79	−0.141415	3.27 (12)	−0.02	3.2824	6, 7, 8
^{74}GeO	−0.14089	−0.140515	—	—	—	6, 7, 8
CO	−0.26910 (20)[c]	—	0.245 (150)	—	0.1098	9, 10
^{14}CO	−0.24664 (20)[c]	—	0.130 (84)	—	—	9
$C^{18}O$	−0.25622 (20)[c]	—	0.064 (118)	—	—	9
^{13}CO	−0.25704 (20)[c]	—		—	—	9
H_2	0.88291 (7)	0.89004[d]	−0.00266 (40)	0.0049	—	11
HD	0.663211 (14)	0.667872[d]	−0.00098 (56)	−0.0063	0	12
D_2	0.442884 (52)	0.445402[d]				13

[a] Uncertainties are 1σ.

[b] g_r has been extrapolated by using $l = 4.74$.

[c] Uncertainties are relative.

[d] g_c has been extrapolated by using $l = 3.7$.

References: 1, Bass *et al.* (1987); 2, de Leeuw & Dymanus (1973); 3, Nelson *et al.* (1960); 4, Lawrence *et al.* (1963); 5, Wharton *et al.* (1960); 6, Davis & Muenter (1974); 7, Honerjager & Tischer (1973); 8, Raymonda *et al.* (1970); 9, Rosenblum *et al.* (1958); 10, Muenter (1975); 11, Harrick & Ramsey (1954); 12, Quinn *et al.* (1958); 13 Barnes *et al.* (1954).

dipole moments obtained from Stark-effect measurements. The LiH and CO *g*-factors have not been extrapolated to their equilibrium values because the extremely aspherical electron clouds result in negative values of g_r, and these molecules would be expected to have a very different dependence of g_r on bond length than HF or H_2. GeO shows a smaller linear dependence on v, which was used to extrapolate g_r (Davis & Muenter 1974). The result for ArH^+ (corrected for vibrational effects based on the recent HF data), $\mu = 1.59 \pm 0.4$ D (1σ), lies just within the 2σ range of the theoretical value of 2.2 D, calculated by Rosmus (1979) with the coupled electron-pair approximation (CEPA) method.

The dependence of g_r on the bond length will be different for each molecule. From (1), g^{nuc} is completely independent of R, and g^{el} determines the R dependence. At short bond lengths, the electron cloud becomes spherical for $^1\Sigma$ molecules, and $g^{el} \rightarrow 0$. For neutral molecules, as the bond stretches to near dissociation, the electron clouds become spherical around their respective nuclei, and $g^{el} \rightarrow -g^{nuc}$, so that $g_r \nrightarrow 0$. However, for ions, there will be a residual charge on one atom near the dissociation limit, and $g_r \rightarrow 0$. For ArH^+ in particular, dissociating to Ar and a proton, g_r very nearly approaches g^{nuc} at large R. Thus, the dependence of g_r on R near dissociation is radically different for ions than neutrals. Measurement of *g*-factors in excited vibrational states would yield information on the redistribution of electronic charge as the bond lengthens. ArH^+ is a tightly bound molecule, and near its equilibrium structure the vibrational dependence of g_r is expected to be similar to HF. An experimental confirmation of the vibrational dependence of g_r would remove the doubt involved in the dipole correction.

The vibrational corrections to the dipole moment are extraordinarily large for hydrides. Upon isotopic substitution of deuterium, the reduced mass changes by about a factor of two, resulting in large changes in zero-point vibrational motion. At the opposite extreme, an isotopic substitution of heavier nuclei such as $H^{13}CO^+$ or $HC^{18}O^+$ would have a much smaller change in zero-point vibration, and the corrections mentioned above would probably be negligible. Hydrides such as ArH^+ have very large *g*-factors, however, making an accurate experimental determination of g_r easier.

The precision of the experimental determination of g_r could be improved both by increasing the magnetic field and by stabilizing the FIR laser. A magnet capable of 10 kG, for example would reduce the error in g_r by a factor of 2.5. The contribution to the error in the dipole moment of ArH^+ would then be 0.15 D (1σ). A magnet capable of producing this field has been constructed, and will be used for future *g*-factor measurements. 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 r.m.s. deviation of the splitting against field was 25 kHz. If the FIR laser could be stabilized to less than 5 kHz for the duration of a single scan, then the line fit should improve to this level of accuracy. Also a slow linear drift of the FIR laser frequency could be eliminated by taking up and down microwave sweeps, and averaging them. With these improvements, the *g*-factor uncertainty should decrease by about a factor of twelve. Even more accuracy can be obtained for heavier molecules by observing lower-frequency transitions because of the decreased Doppler linewidth.

For small *g*-factors that give incomplete splitting of the lines, circular polarization of the radiation can be used to isolate the peaks. This can be accomplished by use of either a quarter wave plate suitable for the absorption frequency, or a polarizing interferometer such as the one used to isolate the sidebands from the laser in the tunable FIR spectrometer. Circular polarization of the radiation also permits determination of the sign of g_r, and thus the sign of the dipole moment. Only one of the $\Delta M = \pm 1$ peaks is observed, and the handedness of the beam can be determined by comparison with a molecule of known g-factor sign, such OCS (Eschbach & Strandberg 1952). In the case of the polarizing interferometer, the beam handedness can be easily decided without a reference molecule.

The Zeeman-effect method for determining electric dipole moments should be applicable to a large number of molecular ions, and the technique has been used to verify the signs of dipole moments for many neutral molecules. In the latter case, a very modest accuracy proves satisfactory because the magnitudes are well known from Stark-effect experiments. If the goal of the experiment is to measure the magnitude as well as the sign, then the accuracy desired for the dipole determines the necessary accuracy for g_r. From (7), the two parameters that determine the uncertainty in μ for a given uncertainty in g_r are Δz, the displacement of the centre of mass upon isotopic substitution, and B, the rotational constant. Larger values of Δz and B reduce the required accuracy in g_r. Table 2 shows the required accuracy in g_r for a 0.1 D uncertainty in μ for various molecular ions and isotopic substitutions. Rosenblum *et al.* (1958) were able to determine the dipole moment of CO to ±0.1 D using microwave spectroscopy, and Davis & Muenter (1974) obtained ±0.12 D accuracy for GeO with molecular-beam techniques. Both of these results agree with the Stark-effect values within experimental error, and the small vibrational correction for GeO (−0.02 D) could result from zero-point changes in the dipole moment. For other molecules, the accuracy is substantially worse, perhaps because of lack of interest. Asymmetric tops present a serious problem at the resolution of conventional rotational spectroscopy, because for a given rotational transition, the different M levels have different splittings. Fitting of lineshapes to sums of unresolved peaks is unlikely to result in the necessary precision for a satisfactory determination of the dipole moment. Unless much higher resolution spectra can be obtained, this technique will be limited to linear and symmetric top molecules.

TABLE 2. REQUIRED PRECISION IN g_r FOR DETERMINATION OF THE ELECTRIC DIPOLE TO ±0.1 D FOR VARIOUS MOLECULAR IONS

(Δz is the displacement of the centre of mass for the given isotopic substitution, B is the rotational constant of the heavier ion, and g_r gives the magnetic moment in nuclear magnetons.)

molecule	Δz/Å[a]	B/GHz	Δg_r for $\Delta\mu = 0.1$ D	$\Delta g_r H\beta_1$ at 10 kG/kHz
ArH^+/ArD^+	0.030	153	0.00038	5.8
HeH^+/HeD^+	0.11	629	0.0057	87
NeH^+/NeD^+	0.043	281	0.0010	15
$H^{13}CO^+/HC^{18}O^+$	0.053	43	0.00019	2.9
$H^{15}NN^+/HN^{15}N^+$	0.037	45	0.00014	2.1
$H^{13}CS^+/HC^{34}S^+$	0.017	21	0.000030	0.46

[a] 1 Å = 10^{-10} m = 10^{-1} nm.

In summary, we have presented the details of the first experimental determination of the dipole moment of a molecular ion. Our current result for the dipole moment of ArH^+, (1.59±0.4 D), lies just within the 2σ error bar of the *ab initio* result of Rosmus (1979). It is shown that rotational spectroscopy can be used to achieve the necessary precision for a reasonable determination (±0.1 D) of the dipole moments of a variety of ions, although extension to asymmetric tops appears unlikely in the near future. Zero-point vibrational effects, which can be substantial for deuterium substitution of hydrides, are likely to be unimportant for other types of molecules.

This work was supported by the National Science Foundation under Grant no. CHE-84-02861. K.B.L. thanks the National Science Foundation for a fellowship. G.A.B. is a Berkeley Miller Research Fellow, 1985–87, and R.J.S. was a Berkeley Miller Research Professor, 1985–86.

REFERENCES

Barnes, R. G., Bray, P. J. & Ramsey, N. F. 1954 *Phys. Rev.* **94** (4), 893.
Bass, S. M., DeLeon, R. L. & Muenter, J. S. 1987 *J. chem. Phys.* **86** (8), 4305.
Betz, A. & Zmuidzinas, J. 1984 In *Proc. Airborne Astr. Symp.* (NASA CP-2353), p. 320.
Bicanic, D. D., Zuidberg, B. F. J. & Dymanus, A. 1978 *App. Phys. Lett.* **32**, 367.
Bowman, W. C., Plummer, G. M., Herbst, E. & DeLucia, F. C. 1983 *J. chem. Phys.* **79**, 2093.
Davis, R. E. & Muenter, J. S. 1974 *J. chem. Phys.* **61** (7), 2940.
DeLucia, F. C., Herbst, E., Plummer, G. M. & Blake, G. A., 1983 *J. chem. Phys.* **78**, 2312.
Eschbach, J. R. & Strandberg, M. W. P. 1952 *Phys. Rev.* **85** (1), 24.
Farhoomand, J., Blake G. A., Frerking, M. A. & Pickett, H. M. 1985 *J. appl. Phys.* **57**, 1763.
Fetterman, H. R., Tannenwald, P. E., Clifton, B. J., Parker, C. D., Fitzgerald, W. D. & Erickson, N. R. 1978 *Appl. Phys. Lett.* **33**, 151.
Gordy, W. & Cook, R. L. 1970 *Microwave molecular spectra.* New York: Interscience Publishers.
Harrick, N. J. & Ramsey, N. F. 1954 *Phys. Rev.* **94**, 893.
Honerjager, R. & Tischer, R. 1973 *Z. Naturf.* A**28**, 1374.
Kaiser, E. W. 1970 *J chem. Phys.* **53**, 1686.
Lawrence, T. R., Anderson, C. H. & Ramsey N. F. 1963 *Phys. Rev.* **130**, 1865.
de Leeuw, F. H. & Dymanus, A. 1973 *J. molec Spectrosc.* **48**, 427.
Martin, D. H. & Puplett, E. 1969 *Infrared Phys.* **10**, 105.
Muenter, J. S. 1975 *J. molec. Spectrosc.* **55**, 490.
Nelson, H. M., Leavitt, J. A., Baker, M. R. & Ramsey, N. F. 1961 *Phys. Rev.* **122**, 856.
Okumura, M., Yeh, L. I., Normand, D., van den Biesen, J. J. H., 1987 Bustamente, S. W., Lee, Y. T., Lee, T. J., Handy, N. C. & Schaefer, H. F. *J. chem. Phys.* **86**, (7), 3807.
Pickett, H. M. 1977 *Rev. scient Instrum.* **48**, 706.
Quinn, W. E., Baker, J. M., LaTourrette, J. T. & Ramsey, N. F. 1958 *Phys. Rev.* **112**, 1929.
Ramsey, N. F. 1952 *Phys. Rev.* **87**, 1075.
Raymonda, J. W., Muenter, J. S. & Klemperer, W. A. 1970 *J. chem. Phys.* **52**, 3458.
Rosenblum, B., Nethercot, A. H. & Townes, C. H. 1958 *Phys. Rev.* **109** (2), 400.
Rosmus, P., 1979 *Theor. chim. Acta* **51**, 359.
Townes, C. H., Dousmanis, G. C., White, R. L. & Schwarz, R. F. 1955 *Disuss. Faraday Soc.* **19**, 56.
Townes, C. H. & Schawlow, A. L. 1975 *Microwave spectroscopy*, New York: Dover Publications.
van Vleck, J. H. 1932 *Theory of electric and magnetic susceptibilities.* Oxford: Clarendon Press.
Wharton, L., Gold, L. P. & Klemperer, W. 1960 *J. chem. Phys.* **33**, 1255.

Discussion

H.-J. FOTH (*University of Kaiserlautern, F.R.G.*). For the example of NCO^-, wherein the bending-mode excitation is much higher than that of the stretching mode, Professor Saykally presented temperatures of 2000 and 700 K, respectively. How big are the uncertainties, and how many vibrational bands have been used for the analysis? What is the rotational temperature?

R. J. SAYKALLY. The vibrational temperatures, as estimated from relative intensities of adjacent fundamental and hot band lines, are probably reliable to about 30%. A total of eight different vibrational states were sampled. Rotational temperatures, extracted from Boltzmann plots in the respective bands, yield an average temperature of 720 K, reliable to about 30%. Because the neutral translational temperature was determined from Doppler profiles to be near 650 K, we again find support for the idea that the ionic rotational temperature is equilibrated with the neutral kinetic temperature, which is hotter than the cell wall because of the finite thermal conductivity of the gas.

E. HIROTA (*Institute for Molecular Science, Okazaki* 444, *Japan*). I am very much impressed by Professor Saykally's success in determining the dipole moment of ArH^+ ion. Does his method allow him to determine the sign of the g_r factor? The sign of the dipole moment depends on the sign of g_r. Which end of ArH^+ does he think is positive?

R. J. SAYKALLY. The sign of g_r can easily be determined by using a quartz $\frac{1}{4}\lambda$ plate that works at *ca.* 600 GHz. One of the $\Delta M = \pm 1$ peaks would vanish when the FIR beam becomes circularly polarized. By comparison with CO, which is known to have a negative g-factor (Rosenblum *et al.* 1958), the sign of the g-factor of ArH^+ can be verified. We have performed this experiment, yielding $g_r > 0$, and thus a dipole moment of polarity–ArH^+.

General reference

Miller, D. J., DeLeon, R. & Muenter, J. S. 1980 *J. molec. Spectrosc.* **83**, 283.

T. OKA, F.R.S. (*University of Chicago, U.S.A.*). How did Professor Saykally obtain the estimated H_3O^+ ion number density of $1\text{–}5 \times 10^{13}$ cm^{-3}? If we assume a current density of, say, 0.2 A cm^{-2}, these very large values correspond to very small electron migration velocity of $10^5\text{–}2 \times 10^4$ cm s^{-1}, even if we assume all cations are H_3O^+.

R. J. SAYKALLY. These densities were actually estimated for the HNN^+ and H_3O^+ ions, generated in H_2–N_2 and H_2–O_2 plasmas. Our current densities are approximately 0.5 A cm^{-2}. With theoretical values for the Einstein coefficients and a value of 500 K for the rotational temperature, we do in fact, get densities more near *ca.* 10^{12} cm^{-3}, as Professor Oka suggests. These values are consistent with those obtained by assuming electron-drift velocities in discharges through H_2 or O_2 ($1\text{–}4 \times 10^6$ cm s^{-1} or $3\text{–}8 \times 10^6$ cm s^{-1} at 2–10 V cm^{-1} Torr^{-1}–v: Engel), which, at our current densities, should result in ion densities on the order of 10^{12} ($0.6\text{–}2.5 \times 10^{12}$ cm^{-3} for H_2 and $3\text{–}8 \times 10^{11}$ cm^{-3} for O_2). However, uncertainties in the vibrational and translational temperatures of the ions and variations in the gas composition can change these estimates by factors of 1–5.