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Can one determine the dipolar moment of $ArH^+X^1\Sigma^+$ from frequency data of pure rotational and vibration-rotational spectra?

J.F. Ogilvie

Department of Mathematics, Centre for Experimental and Constructive Mathematics, Simon Fraser University, 8888 University Drive, Burnaby, BC, Canada V5A 1S6

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Abstract

On the basis of an objective fit to 443 appraised measurements of frequencies and wave numbers of pure rotational and vibration-rotational transitions of ArH^+ in six isotopic variants, 19 fitted parameters – 12 for potential energy and seven for extra-mechanical effects – suffice to reproduce these measurements within experimental uncertainty, $\hat{\sigma} \sim 1$. Careful analysis of these parameters reveals that, whereas a rough estimate of rotational g factor is consistent with both previous experimental and computational results, no sensible estimate of electric dipolar moment is derivable, despite Molski's claim to the contrary [Chem. Phys. Lett. 342 (2001) 293]. Deficiencies of Molski's analysis are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Molski [1] claimed to have determined the electric dipolar moment of ArH^+ from only spectral data – frequencies and wave numbers of pure rotational and vibration-rotational transitions of molecules in the absence of external electric or magnetic field. Because my tests on spectral data for such properties before their provision to Molski [1] indicated no such result, I have reexamined this question by reassembling a data set and undertaking careful analysis of it according to established methods [2,3]. The ultimately compiled set of critically appraised data comprises 443 frequencies and wave numbers of transitions, as specified in Table 1.

To define fitting parameters, we recall this effective hamiltonian of form [3]

$$\mathscr{H}_{\text{eff}} = (-\hbar^2/2\mu)\,\mathrm{d}/\mathrm{d}R\,(1+\beta(R))\,\mathrm{d}/\mathrm{d}R + V(R) + V'(R) + (\hbar^2/2\mu R^2) \times (1+\alpha(R))J(J+1) \quad (1)$$

in which $\hbar$ is Planck's constant h divided by 2π; μ is the reduced mass according to a prescription [18] specifically applicable to molecular ions; for ArH^+ the standard isotopic species is taken to be $^{40}Ar^1H^+$. We apply pertinent radial functions in terms of parameter z for reduced displacement [2]

$$z \equiv 2(R - R_e)/(R + R_e) \quad (2)$$

E-mail address: ogilvie@cecm.sfu.ca (J.F. Ogilvie).

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Table 1
Data of pure rotational and vibration-rotational transitions of ArH^+

Species	Nature of transitions	Lines	Source, Ref.
$^{40}Ar^1H^+$	Pure rotational in $v = 0$	10	[4–6]
	Pure rotational in $v = 1, 2, 3, 4$	4	[6]
	Vibration-rotational with $\Delta v = 1$ and $0 \leqslant v'' \leqslant 4$	140	[7–11]
	Vibration-rotational with $\Delta v = 1$ and $0 \leqslant v'' \leqslant 5$	195	[12]
	Vibration-rotational with $\Delta v = 1$ and $5 \leqslant v'' \leqslant 6$	30	[13]
$^{38}Ar^1H^+$	Vibration-rotational with $\Delta v = 1$ and $v'' = 0$	2	[14]
$^{36}Ar^1H^+$	Vibration-rotational with $\Delta v = 1$ and $v'' = 0$	7	[8,11]
$^{40}Ar^2H^+$	Pure rotational in $v = 0$	16	[4,15–17]
	Pure rotational in $v = 1$	1	[16]
	Vibration-rotational with $\Delta v = 1$ and $0 \leqslant v'' \leqslant 2$	36	[13]
$^{38}Ar^2H^+$	Pure rotational in $v = 0$	1	[15]
$^{36}Ar^2H^+$	Pure rotational in $v = 0$	1	[15]

with R as the instantaneous internuclear distance and R_e as the equilibrium internuclear separation. For a radial function for internuclear potential energy independent of mass

$$V(R) \to V(z) = c_0 z^2 \left(1 + \sum c_j z^j\right), \tag{3}$$

a correction arises [3] to take into account the adiabatic effects.

$$V'(R) \to V'(z) = m_e \left(\sum_{j=1} u_j^{Ar} z^j / M_{Ar} + \sum_{j=1} u_j^{H} z^j / M_H \right). \tag{4}$$

For kinetic energy along the internuclear axis, the corresponding correction for non-adiabatic vibrational effects [3] is

$$\beta(R) \to m_e \left(\sum_{j=1} s_j^{Ar} z^j / M_{Ar} + \sum_{j=1} s_j^{H} z^j / M_H \right) \tag{5}$$

whereas for the term in the hamiltonian for kinetic energy perpendicular to the internuclear axis, or rotational energy, the correction for non-adiabatic rotational effects [3] is

$$\alpha(R) \to m_e \left(\sum_{j=0} t_j^{Ar} z^j / M_{Ar} + \sum_{j=0} t_j^{H} z^j / M_H \right). \tag{6}$$

These corrections yield contributions to term coefficients Z_{kl}^{Ar} and Z_{kl}^{H} that represent extra-mechanical effects to take into account a condition that electrons follow imperfectly one or other atomic nucleus as the latter vibrates and rotates about the centre of mass. The principal term coefficients $Y_{kl} = U_{kl} \mu^{-1/2(k+2l)}$ analogously represent mechanical effects of atomic nuclei and their associated electrons in vibrational and rotational motions with respect to the centre of molecular mass [19]. Eigenvalues [2]

$$E_{vJ} = \sum_{k=0} \sum_{l=0} \left(Y_{kl} + Z_{kl}^{Ar} + Z_{kl}^{H}\right)(v + 1/2)^k [J(J+1)]^l \tag{7}$$

of this hamiltonian for each isotopic species contain as many term coefficients Y_{kl}, Z_{kl}^{Ar} and Z_{kl}^{H} of functions of quantum numbers vibrational v and rotational J as are required to be consistent with coefficients c_j, s_j^{Ar}, s_j^{H}, t_j^{Ar}, t_j^{H}, u_j^{Ar} and u_j^{H} in radial functions up to a particular value of each individual subscript j, according to a fit with maximal statistical significance; further coefficients Y_{kl} and Z_{kl} are assumed to have negligibly small magnitudes and their values are taken as zero, but no assumption is made, or required, about values of further radial coefficients in this list.

Because proper scrutiny of input data is crucial to yield reliable eventual estimates of small parameters, as is subsequently demonstrated, description in some detail of the procedures applied to assess available data of ArH^+ is essential both for an understanding of the ultimate results and as a basis of an answer to the question in the title of this Letter. For vibration-rotational data of $^{40}Ar^1H^+$ that are most numerous, I fitted each band from each source to band parameters to establish objectively a general precision of those lines that became converted to a weight for further fits;

for pure rotational transitions and in those cases in which too few lines were available for this purpose a precision was assigned for each measurement on taking into account information from the source of these data. 379 specified data of $^{40}Ar^1H^+$ fitted with computer program Radiatom [2] required 14 parameters – coefficients $U_{1,0}$, $U_{0,1}$, c_j with $1 \leqslant j \leqslant 10$ and t_1^H and t_2^H. The need for coefficients c_j up to $j = 10$ is consistent with reduction of data of comparable range in v and J by Johns [13] who evaluated significantly coefficients $U_{6,0}$ and $U_{5,1}$; according to Dunham's theory [19] for which eigenvalues in the form of Eq. (7) represent merely an extension to include extra-mechanical effects, $U_{6,0}$ implies finite values of c_9 and c_{10}. For HCl for which available spectra cover a similar range of v and J and which has mechanical and spectral properties comparable with those of $^{40}Ar^1H^+$, pure rotational and vibration-rotational data of only $^1H^{35}Cl$ also require two parameters t_1^H and t_2^H to take into account non-adiabatic rotational effects, related to function $\alpha(R)$ in the hamiltonian, that would otherwise appear to make parameters Y_{kl} with $l > 1$ for centrifugal distortion inconsistent with $Y_{k,0}$ and $Y_{k,1}$ according to Dunham's theory [19]. To an extent practicable, I treated data of $^{40}Ar^2H^+$ analogously, and added those data with 11 additional measurements for isotopic variants containing ^{36}Ar and ^{38}Ar to comprise the total data for a global fit; results appear in Table 2 as fit A.

Iterative techniques to evaluate non-linear parameters require initial estimates of parameters to be fitted. For the purpose of fit A and according to my habitual practice to ensure an objective search for a minimum of a surface in the parameter hyperspace, rough estimates of $U_{1,0}$ and $U_{0,1}$ with generic values [3, p. 238] of c_1 and c_2 were input to

Table 2
Coefficients of radial functions and other molecular parameters of $ArH^+X^1\Sigma^+$

Parameter	Fit A	Fit B	Fit C	Molski [1]
c_0/m^{-1}	17569894.8 ± 38.1[a]	17569894.7 ± 37.2	17569456.3 ± 65.2	17570038 ± 54
c_1	−1.5637156 ± 0.0000165	−1.5637155 ± 0.0000153	−1.563541 ± 0.000027	−1.563771 ± 0.000020
c_2	1.194339 ± 0.000088	1.194339 ± 0.000084	1.194389 ± 0.000146	1.193592 ± 0.000045
c_3	−0.588041 ± 0.00087	−0.588043 ± 0.00076	−0.60446 ± 0.00134	−0.58232 ± 0.00016
c_4	0.19573 ± 0.0056	0.19574 ± 0.0045	0.28152 ± 0.0079	0.21070 ± 0.00089
c_5	0.11241 ± 0.0102	0.11242 ± 0.0095	0.1202 ± 0.0164	−0.1163 ± 0.0025
c_6	−0.6178 ± 0.096	−0.6180 ± 0.086	−2.090 ± 0.152	[0]
c_7	−0.6798 ± 0.41	−0.6788 ± 0.35	5.235 ± 0.61	−0.1521 ± 0.0096
c_8	7.722 ± 0.68	7.721 ± 0.59	−2.029 ± 1.01	0.321 ± 0.013
c_9	−24.384 ± 1.70	−24.38 ± 1.57	−32.22 ± 2.78	[−0.1177]
c_{10}	51.75 ± 12.4	51.766 ± 10.8	155.2 ± 19.0	
s_0^{Ar}	0.477 ± 0.149	0.477 ± 0.147	1.50 ± 0.26	[−0.2460]
s_2^H	−5.760 ± 0.215	−5.760 ± 0.207	−5.305 ± 0.36	
t_0^H	0.77598 ± 0.027	[0.77598]	[0]	0.507 ± 0.012
t_1^H	−0.7287 ± 0.036	−0.7287 ± 0.0153	0.2093 ± 0.027	0.160 ± 0.034
t_2^H	0.7830 ± 0.150	0.7829 ± 0.042	−3.532 ± 0.075	
$u_1^H/10^6\ m^{-1}$	−11.0124 ± 0.47	−11.0123 ± 0.0034	25.8824 ± 0.0059	−6.28 ± 0.21
$u_2^H/10^6\ m^{-1}$	26.477 ± 1.57	26.477 ± 0.030	−19.126 ± 0.054	
$U_{1,0}/m^{-1}\ u^{1/2}$	268829.225 ± 0.304	268829.224 ± 0.297	268825.876 ± 0.520	268830.22 ± 0.41[b]
$U_{0,1}/m^{-1}\ u$	1028.309403 ± 0.000092	1028.309403 ± 0.000092	1028.309447 ± 0.000162	1028.3086 ± 0.0018[b]
$k_e/N\ m^{-1}$	425.79750 ± 0.00096	425.79750 ± 0.00094	425.78690 ± 0.00165	
$R_e/10^{-10}\ m$	1.280372517 ± 0.000000153	1.280372517 ± 0.000000153	1.280372490 ± 0.000000174	1.2803730 ± 0.0000011
$\hat{\sigma}$	0.9981	0.9969	1.7490	0.885
s_0^H				0.603 ± 0.042
s_1^H				1.042 ± 0.097
t_0^{Ar}				−0.180 ± 0.178
$u_1^{Ar}/10^6\ m^{-1}$				4.16 ± 1.46

[a] Each uncertainty signifies one standard error; values within brackets [ ] are constrained in this fit.

[b] These values are calculated from other values in this column, and are not included in Molski's published Letter [1].

Radiatom; during 42 iterations until satisfactory convergence, the sum of squared weighted errors (each a residual divided by its uncertainty) decreased from 4×10^{13} to 418. In this fit, 10 coefficients of correlation between parameters attained magnitudes greater than 0.9, two of them greater than 0.9999; even though adequate numerical precision is maintained during fitting with Radiatom through calculation with 32 decimal digits and a range of exponents $\sim 10^{\pm 4900}$ [2], this condition is undesirable in that it implies lack of independence of parameters and consequent loss of their prospective physical significance. As several such correlation coefficients involved t_0^{H}, in a succeeding fit this parameter was fixed at its value of 0.77958, otherwise with the same initial estimates as for fit A; for these results as fit B in Table 2, no correlation coefficient has a magnitude greater than 0.9, and standard errors of all parameters, but especially t_j^{H} and u_j^{H}, $j = 1, 2$, are decreased relative to corresponding values in fit A. In a further fit with parameters in the same set but with t_0^{H} constrained to zero, results as fit C in Table 2 indicate that all standard errors are increased relative to those in fits A and B; the reduced standard deviation $\hat{\sigma}$ of fit C is markedly increased to 1.75.

Among many and diverse combinations of parameters tested for these fits, only parameters listed for fit A yield a satisfactory fit, for which a criterion is that $\hat{\sigma}$ is near unity. Of these parameters, $U_{1,0}$, $U_{0,1}$, c_j with $1 \leqslant j \leqslant 10$, s_0^{Ar}, s_2^{H}, t_j^{H} with $0 \leqslant j \leqslant 2$, u_1^{H} and u_2^{H} are independently fitted, and other quantities listed in the table are derived therefrom. Thus 19 parameters suffice to reproduce satisfactorily 443 spectral measurements of frequencies and wave numbers of spectral lines according to Table 1. Before s_2^{H} was introduced into the set of tested parameters, measurements for all lines of $^{40}\mathrm{Ar}^2\mathrm{H}^+$ involving vibrational states beyond $v = 1$ showed a systematic shift: to rectify this condition, s_2^{H} is an obvious remedy because it is primarily associated with $Z_{2,0}$, itself related to $Y_{2,0}$ or $\omega_e x_e$; no other parameter tested resolved that manifest deficiency. The resulting value of s_2^{H} is highly significant: $|s_2^{\mathrm{H}}/\delta s_2^{\mathrm{H}}| = 5.760/0.215 \sim 27$. Only one parameter to take into account extra-mechanical effects associated with Ar is evaluated significantly; among various parameters tested, s_0^{Ar} proved best defined, but even then $|s_0^{\mathrm{Ar}}/\delta s_0^{\mathrm{Ar}}| = 0.477/0.149 \sim 3$, so conveying only marginal significance. Attempts to fit multiple parameters for Ar generated an error message that a specified parameter was ‘linearly dependent upon previous parameters’; as data for isotopic species of Ar other than $^{40}\mathrm{Ar}$ number only 11, and as they involve vibrational states up to only $v = 1$, this condition is understandable. Of other parameters that appear poorly evaluated in fit A, c_7 must be retained in the fit according to a non-linear occurrence, in expressions for Y_{kl} in the eigenvalues, of these parameters c_j for potential energy before c_{10}; no such requirement pertains to parameters s_j, t_j or u_j because they appear only linearly in expressions for Z_{kl} in the eigenvalues [2].

Results of fits A, B, C and others demonstrate clearly that fitted parameters must include t_0^{H} and that its value possesses modest statistical significance. 379 data, including some duplicated transitions from independent measurements, of $^{40}\mathrm{Ar}^1\mathrm{H}^+$ alone require 14 parameters; 53 data added for $^{40}\mathrm{Ar}^2\mathrm{H}^+$ require four further parameters, and 11 additional data for species containing $^{36}\mathrm{Ar}$ and $^{38}\mathrm{Ar}$ require one additional parameter, although evaluated with marginal significance. Because for each subset the weighting of individual and collective measurements on an objective basis ensures that a reduced standard deviation of the fit is almost exactly unity, the data set is well tempered. Under conditions with data from various spectral regions and from sundry laboratories with independent calibration and techniques of measurement, parameters in a set named fit A are judged to be optimal.

What values of further molecular properties can we deduce from values of parameters according to fit A in Table 2? Relations [3,18] between $t_0^{\mathrm{Ar,H}}$ and rotational g factor g_{r} and electric dipolar moment p_0, the latter quantities evaluated at $R = R_{\mathrm{e}}$, or analogously between $s_0^{\mathrm{Ar,H}}$ and vibrational g factor g_{v} and derivative of electric dipolar moment p_1, the latter quantities also evaluated at $R = R_{\mathrm{e}}$, are clearly inapplicable because only one parameter, s_0^{Ar} or t_0^{H}, is evaluated in each case. As parameter s_0^{Ar} is evaluated so poorly, further consideration of it is fruitless. For reasons already described, the statistical significance of parameter t_0^{H} is also questionable, but one might investigate tentatively on the basis of its value in fit A. Scrutiny of relations [3,20]

$$p_0 = \tfrac{1}{2} e R_e \left(t_0^{\mathrm{H}} - t_0^{\mathrm{Ar}} \right), \tag{8}$$

$$g_r = m_p \left(t_0^{\mathrm{H}} / M_{\mathrm{H}} + t_0^{\mathrm{Ar}} / M_{\mathrm{Ar}} \right) \tag{9}$$

indicates that an estimate $g_r = 0.759 \pm 0.027$ is practicable for $^{40}\mathrm{Ar}^1\mathrm{H}^+$ from Eq. (9) with $t_0^{\mathrm{Ar}} = 0$, because division of t_0^{Ar} by M_{Ar} with the latter quantity $\sim$40 u, whereas $M_{\mathrm{H}} \sim 1$ u, makes this calculation of g_r insensitive to a value of t_0^{Ar} in a reasonable range $[-1, 1]$; an extreme value in the latter range would alter g_r by one standard error. Because t_0^{Ar} is indeterminate, p_0 that arises from a direct difference with t_0^{H} in Eq. (8) is likewise absolutely indeterminate. Values of $p_0/10^{-30}$ C m for $^{40}\mathrm{Ar}^1\mathrm{H}^+$ in vibrational state $v = 0$ from experiment are 4.67 ± 1.33 [21], 5.30 ± 1.33 [22], 9.47 ± 1.33, 9.84 ± 1.33 and 11.2 ± 1.33 [23], with a vibrational correction $+0.40 \pm 0.03$ [24]; Gruebele et al. [24] allude to still another value $p_0/10^{-30}$ C m $= 3.00 \pm 1.33$, also for $v = 0$, all from the same experiment. Experimental values of g_r applicable at R_e are 0.6668 ± 0.0034 or 0.6791 ± 0.0034 [23]. Quantum-chemical computation [25] of these quantities yields values of $p_0/10^{-30}$ C m in a range $[6.87, 7.31]$ that might indicate an uncertainty from calculation of this type, and of g_r in a range $[0.6830, 0.6874]$; the former range is consistent with the result $p_0/10^{-30}$ C m $= 7.34$ of a previous computation [26]. Our estimate $g_r = 0.759 \pm 0.027$ from analysis of frequency data hence differs from both previous experimental and computational values, essentially in agreement with one another, by about three standard errors. Worth bearing in mind is a fact that, before weights of data of wave numbers and frequencies of transitions of $^{40}\mathrm{Ar}^1\mathrm{H}^+$ and $^{40}\mathrm{Ar}^2\mathrm{H}^+$ were properly balanced to yield unit reduced standard deviation of separate fits, a global fit of these data yielded $t_0^{\mathrm{H}} \sim 0.884$, thus leading to g_r about eight standard errors from both previous experimental and computational values.

In his analysis of 431 frequencies and wave numbers of rotational and vibration-rotational transitions, Molski [1] claims to fit these data with 19 parameters, 16 adjusted and three constrained, to yield a reduced standard deviation of $\hat{\sigma} = 0.885$, included in Table 2 for comparison. The latter value of $\hat{\sigma}$ implies by its significant difference from unity that data were not properly appraised for their uncertainties to provide weights for a global fit, even though our tests indicate that this treatment has a crucial effect on subsidiary parameters such as s, t and u, and even on higher coefficients c_j for potential energy. For potential energy his fit includes coefficients up to only c_9, even though independent evidence [13] indicates that coefficients up to c_{10} are required for adequate fit. His value of c_9 is not even deduced from observed spectra but is imposed to yield the correct limit of energy at dissociation. Functions $V(z)$ in fit A and from Molski show almost indistinguishable plots in the range of energies defined from spectra; whereas $V(z)$ for my function becomes large as z or R becomes large – because c_{10} has a positive value, Molski's function increases to an unphysical maximum $\sim 14 D_e$ at $\sim 23 R_e$ before decreasing to its constrained asymptotic value D_e as $R \to \infty$. As a function for potential energy is in any case an artefact of a calculational method, not a direct experimental observable, what matters is its capability, in combination with auxiliary radial functions for extra-mechanical effects, to reproduce experimental data, namely frequencies of spectral transitions. Principally because of lack of c_{10} and an irrelevant value of c_9, when Molski's parameters are substituted into equations for Y_{kl} and Z_{kl} to generate eigenvalues according to Eq. (7), the corresponding deviations between observed and calculated frequencies $\nu = E_{v'J'} - E_{v''J''}$ are hundreds of times the experimental uncertainties of measurements; Molski's parameters have clearly no meaning beyond his own computer program. In contrast, parameters from fit A substituted into equations for Y_{kl} and Z_{kl} that are readily available [2,27] or can be easily generated [28] reproduce satisfactorily experimental data within the range of v and J upon which these parameters are based.

Molski [1] presented values of three parameters, of diverse nature – s_0^{Ar}, t_0^{Ar} and u_1^{Ar}, deduced from at most 11 spectral data involving transitions of species containing $^{36}\mathrm{Ar}$ or $^{38}\mathrm{Ar}$, of which one of these was constrained according to his Eq. (18) [1]

which is incorrect; the correct relation, from a trivial rearrangement of published formulae [18], is

$$s_0^{\mathrm{Ar}} = s_0^{\mathrm{H}} + t_0^{\mathrm{Ar}} - t_0^{\mathrm{H}} + t_1^{\mathrm{Ar}} - t_1^{\mathrm{H}} \tag{10}$$

but is inapplicable to his data because a value of t_1^{Ar} is lacking. His value $t_0^{\mathrm{Ar}} = -0.180 \pm 0.178$, crucial to his derivation of properties, is statistically meaningless, and u_1^{Ar} scarcely less although it plays no direct role in further development. Attempts to apply Radiatom [2] to evaluate multiple extra-mechanical coefficients for Ar fail because this program includes a fitting engine with a proper statistical and computational basis [29] that tests for linearly dependent parameters, whereas a bisection algorithm in Molski's program [30] makes no such test. Furthermore, although Molski calls his procedure 'deformationally self-consistent', in applying it for analysis of spectra of NaCl [30] he included four coefficients c_j, beyond those that can be evaluated with available spectral data, with zero values in expressions $Y_{k,0}$, so that his procedure becomes deformationally inconsistent in relation to Dunham's formulation [19]. Whether extra parameters c_j with value zero, not mentioned in publications before that on NaCl but nevertheless practised [30], are included in this work on ArH$^+$ is unknown. For Molski's program to converge requires initial estimates of parameters near ultimate converged values, unlike Radiatom [2] for which only a few non-zero values – and then only rough values – of parameters are invariably provided as input. Comparison of standard errors associated with values of R_e from fit A with Molski's value, in Table 2, indicates that strong but unreported correlations must exist between Molski's parameters; stated standard errors of my values of R_e and k_e include uncertainties in values of Planck's and Avogadro's constants. Although fits of data of only ^{40}Ar^{1}H$^+$ prove that two parameters t_1^{H} and t_2^{H} are required in a meaningful set, Molski deduced a value of only t_1^{H}. Molski deduced $g_r = 0.502 \pm 0.013$ and $p_0/10^{-30}$ C m $= 7.07 \pm 1.83$; the latter value he compared with an older computational value 7.34 ± 0.33 [26]. In any case an analysis based on three values s_0^{Ar}, t_0^{Ar} and u_1^{Ar} must be fundamentally unsound, as coefficients of correlation between these parameters would indicate [24]; such coefficients are not mentioned by Molski [1].

Optimum conditions for the evaluation of molecular electric and magnetic properties from precise frequency data in absence of external applied field require comparably abundant data of isotopic species of both atomic types – Ar and H in the case of ArH$^+$ – and consistent spectra up to comparable energies for all isotopic variants. These conditions apply for GaH, for instance, but not for ArH$^+$ – cf. Table 1: although data of GaH are available for only vibration-rotational transitions [31,32], data for both ^{69}Ga^{1}H and ^{71}Ga^{1}H reach $v' = 5$, whereas data for both ^{69}Ga^{2}H and ^{71}Ga^{2}H reach $v' = 7$; these upper states have indeed comparable energies. Although these data emanate from two laboratories and are measured in disparate experiments, all these data are consistent. With data of such quality we [20] evaluated $g_r = -3.223 \pm 0.011$ for ^{69}Ga^{1}H, with which Sauer's subsequent quantum-chemical computations [33] that yield values in a range $[-2.9457, -3.4440]$ are consistent. In a calculation, based on the same data [31,32] according to my published approach [20], Molski obtained $g_r = -4.2535 \pm 0.0046$ [34] with a purported rotational dependence that is incredibly large. In a further calculation with the same spectral data after Sauer's paper [33] appeared, Molski reported [35] $g_r = -3.493 \pm 0.061$ – hence with a standard error much increased from both that attached to his previous value and that associated with our value [20], which he compared with a selected quantum-chemical value $g_r = -3.4440$ [33]; explanation for a revision of his value is lacking.

In conclusion, careful analysis of all accessible spectral data of ArH$^+$ indicates that a rough value of rotational g factor for ^{40}Ar^{1}H$^+$ might be deducible, but no significant value of electric dipolar moment. Molski's alleged value [1] of dipolar moment is at best fortuitous, and is thus an absolutely unreliable test of other experimental or computational data.

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