Experimental and Theoretical Estimates of the Rotational g Factor of AlH in the Electronic Ground State $X^{1}\Sigma^{+}$

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The rotational g factor of AlH in the electronic ground state $X^1\Sigma^+$ is estimated experimentally from nonadiabatic rotational effects in published vibration-rotational spectra of AlH and AlD measured in the absence of an external electric or magnetic field. This experimental value -2.8 ± 0.5 agrees roughly with the result -3.4 of computations of molecular electronic structure at the level CCSDPPA of theory. According to this rotational g factor from experimental data, the perpendicular component of the paramagnetic contribution to the magnetizability is calculated to be 6.9×10^{-28} J T⁻²; this value is combined with a theoretical estimate of the diamagnetic contribution. The perpendicular component (0.4×10^{-28} J T⁻²) of the total magnetizability is found to be paramagnetic, providing the first indirect experimental evidence for the postulated paramagnetism of the isovalent molecule BH.

Introduction

A free but not rotating diatomic molecule in an electronic state ${}^{1}\Sigma^{+}$ is nonmagnetic in the sense that it lacks a permanent magnetic dipolar moment apart from that associated with intrinsic nuclear angular momenta. Molecular rotation about the center of mass generates a small magnetic dipolar moment that is proportional to the rotational angular momentum and that produces splittings of lines due to rotational transitions when the sample is subjected to an external magnetic field.¹ The rotational g factor that is proportional to the ratio of the magnetic dipolar moment to the molecular rotational angular momentum is the quantity that indicates the extent of the splitting of rotational energies. This Zeeman effect is small but useful; for instance, the isotopic dependence of g_J enables one to determine not only the absolute sign (with respect to internal nuclear coordinates) of the electric dipolar moment and its approximate magnitude² but also the paramagnetic contribution to the magnetizability.³ The rotational magnetic dipolar moment indicates the extent to which the electrons possess net angular momentum apart from their rotation with the nuclear frame.⁴ For this reason the rotational g factor is a measure of nonadiabatic effects, the failure of electrons to follow exactly the motion of the associated nuclei. Besides nonadiabatic rotational and vibrational effects, which reflect the inertia of electrons with respect to the rotational and vibrational motions of the nuclei, respectively, there are adiabatic effects that arise because the internuclear potential energy depends on not only the distance between the nuclei but also their relative momenta, hence their masses. All these effects are commonly associated with partial failure of the approximate separation of electronic and nuclear motions according to which Born and Oppenheimer introduced into-indeed imposed upon-quantum mechanics the classical notion of molecular structure.5 Although van Vleck described in detail the nature of adiabatic and nonadiabatic effects,⁶ he made no reference to the rotational gfactor.

Almost all experiments to determine the rotational g factor involved spectral measurements and the Zeeman effect on rotational transitions in the microwave region or on hyperfine transitions in the radio-frequency region.⁷ The use of the Zeeman effect in relation to the intensities of vibration-rotational transitions enables rough estimates of the rotational g factor through magnetic vibrational circular dichroism, for instance for HCl.⁸ An estimate of the rotational g factor of CO₂ was based on only measured wavenumbers of vibration-rotational transitions of diverse isotopic variants;⁹ the value deduced was the same (within modest error) as that from measurements at radio frequencies on molecular beams in an external magnetic field.¹⁰ Here we relate our estimate of the rotational g factor of the free diatomic molecule AlH purely from measurements of wavenumbers of vibration-rotational transitions of ²⁷Al¹H and ²⁷Al²H to results of computations of molecular electronic structure. From analysis of available spectra we succeeded to evaluate separately to some extent the adiabatic and nonadiabatic effects, based on an analytic treatment of these effects on vibration-rotational energies of diatomic molecules.¹¹

The electronic contribution to the rotational g factor is proportional to the paramagnetic contribution to magnetizability with the center of mass as gauge origin.³ As the remaining nuclear contribution depends on only the molecular geometry, theoretical estimates of the rotational g factor are readily obtained from calculations of the magnetizability;^{12,13} conversely experimental values of the magnetizability are derived from measured rotational g factors. On the basis of calculations of electronic structure, Lipscomb and co-workers predicted¹⁴ about 30 years ago that the isovalent molecule BH possesses net paramagnetism, independent of temperature. Although not net paramagnetic, AlH was later predicted to have a positive perpendicular component of magnetizability.¹⁵ These predictions were supported by other and more accurate calculations,13 but no experimental value is yet known. The magnetizability derived in the present work from the experimental estimate of the rotational g factor is thus the first experimentally based value for AlH and may thereby provide indirect evidence of the paramagnetism of BH.

Analysis of Molecular Spectra

The estimate of the rotational g factor, or g_J , of AlH we derive from analysis of vibration-rotational spectra of ${}^{27}Al^{1}H$ and ${}^{27}Al^{2}H$ according to methods recently refined.¹⁶ Based on a rigorous analytic theoretical treatment¹¹ of the applicable

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adiabatic and nonadiabatic effects, an algorithm was implemented to accept as primary input the atomic masses, vibrational and rotational quantum numbers, and wavenumbers of transitions of diatomic molecules. According to the algorithm, the program Radiatom evaluates, to the maximum practicable extent depending on the quality and quantity of pertinent available data, the coefficients of the applicable radial functions, namely, those describing the variation with internuclear distance of internuclear potential energy independent of nuclear mass V(R), of adiabatic effects V'(R), and of nonadiabatic rotational $\alpha(R)$ and nonadiabatic vibrational $\beta(R)$ effects for the distinct atomic nuclei if data of isotopic variants are available. By this means we evaluate parameters in the effective Hamiltonian for nuclear motion that has the form^{11,16}

$$\mathcal{H}_{eff} = \hat{P}[1 + \beta(R)]\hat{P}/2\mu + V(R) + V'(R) + hcB_e[1 + \alpha(R)]J(J+1)R_e^2/R^2$$
(1)

For purposes of actual use of these functions we transform to the reduced displacement variable z in terms of the instantaneous R and equilibrium R_e internuclear distances,

$$z = 2(R - R_{e})/(R + R_{e})$$
 (2)

Henceforth with units of wavenumber assumed for appropriate quantities in conformity with spectral conventions and with SI units, we represent the potential energy formally independent of nuclear mass in the form

$$V(z) = c_0 z^2 (1 + \sum_{j=1}^{j} c_j z^j)$$
(3)

For an assumed diatomic molecule AB having nuclei of unlike protonic numbers, the remaining functions dependent on individual nuclear masses we represent by means of separate expansions for the nucleus of each type a and b; for nonadiabatic vibrational effects,

$$\beta(R) = m_{\rm e} \left[\sum_{j=0}^{s} s_j^{\rm a} z^j / M_{\rm a} + \sum_{j=0}^{s} s_j^{\rm b} z^j / M_{\rm b} \right]$$
(4)

for nonadiabatic rotational effects,

$$\alpha(R) = m_{\rm e} \left[\sum_{j=0}^{a} t_j^{a} z^j / M_{\rm a} + \sum_{j=0}^{b} t_j^{b} z^j / M_{\rm b} \right]$$
(5)

and for adiabatic effects (combined with residual nonadiabatic vibrational or other effects with the same dependence on mass¹¹),

$$V'(R) = m_{\rm e} \left[\sum_{j=1}^{a} u_j^{a} z^j / M_{\rm a} + \sum_{j=1}^{b} u_j^{b} z^j / M_{\rm b} \right]$$
(6)

The molecular energies within a particular electronic state, or vibration-rotational terms, we express in the form extended from Dunham's systematic relation¹⁷ (that influenced also van Vleck⁶)

$$\tilde{E}_{vJ} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} (Y_{kl} + Z_{kl}^{r,a} + Z_{kl}^{r,b} + Z_{k}^{lv,a} + Z_{kl}^{v,b}) \times (v + \frac{1}{2})^{k} (J^{2} + J)^{1} (7)$$

in which term coefficients Y_{kl} depend in a nonlinear manner on only the equilibium internuclear separation R_e , the equilibrium force coefficient k_e , the reduced mass μ , and coefficients c_j in the radial function 3 for potential energy. For the vibration-rotational consequences of adiabatic and nonadiabatic effects, additional term coefficients Z_{kl}^v of each nucleus a or b depend separately on the preceding parameters plus coefficients s_j^a , u_j^a , and M_a or s_j^b , u_j^b , and M_b , respectively, whereas for further rotational effects the coefficients Z_{kl}^r of nucleus a or b depend on parameters in the first group plus s_j^a , t_j^a , and M_a or s_j^b , t_j^b , and M_b , respectively. In eq 7 the explicit dependences of E_{vJ} , Y_{kl} , and the various Z_{kl} on the isotopic variant are suppressed. Fitting the experimental differences $\bar{\nu} = \tilde{E}_{v'J'} - \tilde{E}_{vJ}$ between the spectral terms to the parameters, the pertinent coefficients of the radial functions, expressions 3-6, was based on analytic functions^{11,16} of term coefficients Y_{kl} and various Z_{kl} in eq 7 in terms of these parameters.

In the absence of pure rotational transitions, experimental data comprise the known infrared spectra of AlH and AlD according to the following sources. Vibration-rotational transitions of AlH in emission¹⁸ consist of lines in the P and R branches of bands containing the first overtone and others in the sequence $\Delta v=2$ up to v'=8; to measure these spectra, an interferometer of broad spectral range and adequate sensitivity concurrently at a spectral resolution 1.8 m⁻¹ detected transitions of significant intensity within the range 2400 $< \tilde{\nu}/10^2 \text{ m}^{-1} < 3300$. Transitions of AlD in absorption¹⁹ comprise lines in the P and R branches of the fundamental band and others in the sequence $\Delta v=1$ up to v'=7; although the effective resolution of laser diodes operated as sources for these measurements was less than 0.1 m⁻¹, the characteristic performance of these diodes left spectral gaps in the wavenumber range within which relatively intense lines were not detected. Lines of AlH were similarly measured²⁰ in the sequence $\Delta v=1$ up to v'=4. Numerous lines due to emission of both AlH, in the sequence $\Delta v=1$ up to v'=5, and AlD, in the sequence $\Delta v=1$ up to v'=7, were measured with an interferometric spectrometer.²¹ In our analysis we combined all these data with appropriate weights.

Further explanation of incorporation of these data into our analysis is appropriate. In accordance with the description by the authors,¹⁸ the uncertainties of most lines in the sequence $\Delta v=2$ of AlH were set to be 0.3 m⁻¹, except for weak, overlapped, or blended lines (identified by these authors), in which case the uncertainties were set as much as 300 m⁻¹. The uncertainty of almost all lines of AID measured in absorption¹⁹ was set to be 0.08 m⁻¹; although the authors specified a nominal accuracy 0.10 m⁻¹,¹⁹ the quality of the fitting results indicated that in general the latter value was slightly conservative, but a few outliers, discernible in the original analysis, 19 were assigned uncertainties 0.8 or 8.0 m⁻¹. Of 22 lines of AlH measured with a laser diode as source,²⁰ all wavenumbers except one were assigned an uncertainty 0.2 m⁻¹; four lines had relatively large residuals within the tolerated range. Of 734 lines reported for AlH and AlD in emission,²¹ two were rejected outright as having excessively large residuals; these lines at 155 959.62 and 156 057.647 m^{-1} may belong to H₂O. Although the precision of measurement of intense lines in this collection²¹ was claimed to be measured to be 0.02 m⁻¹, preliminary fits indicated by systematic conformity of most residuals within a smaller variation that this value had been estimated conservatively; for this reason the uncertainty of 552 lines was set to be 0.01 m⁻¹, with 43 lines at 0.02 m⁻¹, 57 lines at 0.03 m⁻¹, and the remainder at larger values, generally 0.05, 0.2, 0.5, or 2.0 m⁻¹ (generally as the authors²¹ indicated), so that discrepancies failed to affect significantly the quality of the fit. In procedures of nonlinear regression with analytic expressions for the spectral terms and for derivatives of the residuals with respect to parameters according to the criterion of the minimum sum of squares of the residuals, the weight of each line was assigned to be the reciprocal square of the uncertainty. The results of the best fit appear in Table 1.

Various sets of trial parameters were tested to attain the maximum F value; because this parameter takes into account not only the standard deviation of the fit but also the number of parameters in the model, it is thus an objective criterion of the relative goodness of fit, even though statistical significance of the F value may be less well defined in nonlinear regression than in linear regression. Because there was no variation of the mass of Al, this element having only one naturally occurring stable nuclide

TABLE 1: Coefficients of Radial Functions and Other Molecular Properties of AlH X $^{1\Sigma^{+}}$

j	c _j	tj ^H	$u_{f}^{\rm H}/10^{6} {\rm m}^{-1}$		
0	$(11\ 058\ 156.44 \pm 0.57)\ m^{-1}$	$[-2.8 \pm 0.5]$			
1	$-1.280\ 233\ 9\pm 0.000\ 001\ 3$	6.9146 ± 0.0111	-18.1979 ± 0.0047		
2	0.805 089 0 ± 0.000 008 0	-8.524 ± 0.32	20.5737 ± 0.0135		
3	-0.289 319 ± 0.000 050	3.629 ± 0.62	-14.45 ± 1.14		
4	0.037 84 ± 0.000 25		19.89 ± 4.8		
5	0.004 73 ± 0.000 95				
6	-0.3435 ± 0.0040				
7	0.3364 ± 0.0126				
8	0.601 ± 0.039				
9	-2.752 ± 0.143				
	$U_{1,0}/m^{-1} u^{1/2} = 165\ 961.3188 \pm 0.0089$ $U_{0,1}/m^{-1} u = 622\ 688\ 770 \pm 0.000\ 099$				
	$k_{\rm c}/N {\rm m}^{-1} = 162.279.734 \pm 0.000.097$				

 $\vec{R_e}/10^{-10} \text{ m} = 1.645 366 92 \pm 0.000 001 39$ range of validity $1.24 \leq R/10^{-10} \text{ m} \leq 2.6$ ^a Each stated uncertainty represents one estimated standard error; the normalized standard deviation of the fit of 1201 data was 1.26 and the

F value was 3.47×10^{15} ; the value of $t_0^{\rm H}$ was constrained in the final fit.

²⁷Al, the value of t_0^{Al} was constrained to zero. For the same reason all values of other coefficients t_j^{Al} and u_j^{Al} , j > 0, had to be constrained to zero; to this extent the potential-energy coefficients c_j absorb adiabatic and nonadiabatic effects associated with Al and must therefore be considered merely effective parameters applicable to only ²⁷Al. All fits in which the parameter $t_0^{\rm H}$ was freely varied yielded relatively large magnitudes of correlation coefficients linking this parameter to $t_1^{\rm H}$, $u_3^{\rm H}$, and $u_4^{\rm H}$; the principal reason for this strong correlation is lack of isotopic variants of Al, such that μ was inevitably strongly correlated with $M_{\rm H}$. In particular, the sum $t_0^{\rm H} + t_1^{\rm H}$ was well defined, namely, 4.1146 \pm 0.0111, although t₀^H was separately defined poorly. For this reason t_0^{H} was fixed at values varied in the range [-4, 3] and other parameters were then freely fitted, with a constant set of initial estimates (rounded values of $U_{1,0}$, $U_{0,1}$, c_1 , c_2 and c_3 and zero otherwise); under these conditions the F value showed a weak maximum at $t_0^{\rm H} = -2.8$, and the uncertainty associated with this maximum was about 0.5. For 1201 transitions, only 19 nonzero parameters were required to yield a normalized standard deviation 1.26; the latter value is slightly greater than unity but still acceptable in view of the disparate sources of data. The maximum range of validity of the associated radial functions is $1.24 \leq R/10^{-10}$ m ≤ 2.60 , corresponding approximately to classical turning points of vibrational state v = 8 of AlH of greatest energy to which vibrationrotational transitions were measured.18

We seek to relate the value of $t_0^{\rm H}$ to the rotational g factor, or g_J , that is proportional to the magnetogyric ratio; the latter quotient of the induced rotational magnetic dipolar moment and the rotational angular momentum is a measure of the extent of splitting, according to M_J , of the energy of a particular vibrationrotational state (for J > 0). The factor g_J is thus an expectation value $\langle vJ|\alpha(R)|vJ\rangle$ or $\langle vJ|g_J(R)|vJ\rangle$ of a particular state denoted by vibrational quantum number v and rotational quantum number J. For a net electrically neutral diatomic molecule of relative electric polarity ⁺AB⁻, the g factor has two contributions, $g_J^{\rm na}$ attributed to interaction between electronic and nuclear motions and the other from the rotating electric dipolar moment μ_e (at equilibrium internuclear distance R_e):²²

$$g_{J} = g_{J}^{na} + m_{p} \left(M_{a}^{-1} - M_{b}^{-1} \right) \mu_{e} / (eR_{e})$$
(8)

in which m_p is the mass of the proton and e its charge. The equations²³ for partition of the g factor into contributions of the separate atomic centers thus become

$$t_0^{a} = \mu [g_J/m_p + 2\mu_e/(eR_eM_b)]$$
(9)

$$t_0^{b} = \mu[g_J/m_p - 2\mu_e/(eR_eM_a)]$$
(10)

Although the electric dipolar moment of AlH has never been determined experimentally, its magnitude is expected to be relatively small, about 7×10^{-31} C m;²⁴ thus the magnitude of the factor $[2\mu_e/(eR_e)]$ is ~0.04. For this reason, whether the polarity of AlH is +AlH- or -AlH+ is immaterial; the value of g_J of ²⁷Al¹H remains essentially the same as that of $t_0^{\rm H}$, hence about -2.8. For the same reason, the value of $t_0^{\rm Al}$ would also be about -2.8; because the latter coefficient appears in vibration-rotational terms as $t_0^{\rm Al}/M_{\rm al}$ with $M_{\rm al} \sim 27$, its effect on the spectral terms is much smaller than that of $t_0^{\rm H}$, which enters as $t_0^{\rm H}/M_{\rm H}$ with $M_{\rm H} \sim 1$ for H or 2 for D.

Calculations of Molecular Electronic Structure

The rotational g factor is in general a tensor property, but for a linear molecule with nuclei along the z axis the elements g_{xx} and g_{yy} are equal and considered to be g_J , whereas g_{zz} and all off-diagonal elements are zero.¹ This factor consists of a nuclear part and an electronic part³

$$\mathbf{g}_J = \mathbf{g}_J^{\mathrm{nu}} + \mathbf{g}_J^{\mathrm{el}} \tag{11}$$

in which

$$g_J^{nu} = (m_p/I) \sum_{k=1}^2 Z_k R_{z,k}^2$$
 (12)

and

$$g_{J}^{el} = [2m_{p}/(m_{e}I)] \sum_{n \neq 0} \langle 0|l_{\perp}(\mathbf{R}_{CM})|n\rangle \langle n|l_{\perp}(\mathbf{R}_{CM})|0\rangle / (E_{0}-E_{n})$$
(13)

here I is the inertial tensor, $R_{z,k}$ is the z component of the position vector of nucleus k, Z_k is the charge of nucleus k in units of the protonic charge, and $I_{\perp}(\mathbf{R}_{CM})$ is the perpendicular component of the operator for electronic angular momentum with respect to the center of mass; E_0-E_n is the difference between the energy of the electronic ground state $|0\rangle$ and the energy of an electronically excited state $|n\rangle$. The nuclear part is determined by only the nuclear masses and internuclear distance, whereas the electronic part is related to the paramagnetic contribution to the magnetizability ξ^p evaluated with the gauge origin being the center of mass

$$g_J^{\text{el}} = -4m_p m_e \xi_l^{\text{p}}(\mathbf{R}_{\text{CM}}) / [e^2 I]$$
(14)

The total magnetizability is evaluated by means of the rotational g factor and the diamagnetic contribution

$$\xi_{\perp}(\mathbf{R}_{\rm CM}) = \xi_{\perp}^{\rm d}(\mathbf{R}_{\rm CM}) - e^2 I g_J^{\rm el} / [4m_{\rm e}m_{\rm p}] \qquad (15)$$

Expressions such as eq 13 can be evaluated elegantly by means of propagator methods.²⁵ Electron correlation is introduced into these methods according to either Møller–Plesset perturbation theory²⁶ or a multiconfigurational approach.²⁷ In the present work we applied the coupled-cluster singles-and-doubles polarization-propagator approximation (CCSDPPA).²⁸ which provides satisfactory agreement with experimental values of various molecular properties of a quasidegenerate system such as AlH.²⁹ Using basis set 106¹³ and the internuclear distance in Table I, we derived for the rotational g factor at R_e the value -3.370.

To estimate the vibrational and rotational dependences of the rotational g factor, we calculated it at 12 internuclear distances in the range $1.277 < R/10^{-10}$ m < 2.02; the results appear in Table 2. Numerical integration of the interpolated radial function of the rotational g factor over the wavefunction for the ground

 TABLE 2:
 Values of g_J at Varied Internuclear Separation

 Calculated at the Level CCSDPPA of Theory

<i>R</i> /10 ⁻¹⁰ m	gj	<i>R</i> /10 ⁻¹⁰ m	gj
1.2774	-6.1120	1.6480	-3.3581
1.3832	-5.0557	1.7007	-3.1258
1.4890	-4.2490	1.7536	-2.9179
1.5420	-3.9159	1.8066	-2.7322
1.5949	-3.6210	1.9124	-2.4177
1.6454	-3.3704	2.0182	-2.1660
1.6478	-3.3590		

vibration-rotational state,³⁰ which was obtained from a separate electronic calculation of the potential-energy curve,³¹ yielded the expectation value $\langle 0,1|g_J|0,1 \rangle$ for the state with v=0 and J=1. As expected, this calculated expectation value $g_J=-3.295$ differs only slightly from the value of g_J at R_e . Alternatively one can expand the vibration-rotational expectation value³² of the rotational g factor as

$$\langle vJ|\mathbf{g}_{J}|vJ\rangle = \langle vJ|\sum_{j=0} \mathbf{g}_{j}z'|vJ\rangle = \sum_{j=0} \mathbf{g}_{j}\langle vJ|z'|vJ\rangle = \mathbf{g}_{0} + \sum_{j=1} \mathbf{g}_{j}\langle vJ|\mathbf{g}_{J}|vJ\rangle \approx \mathbf{g}_{0}$$
(16)

in which each expectation value $\langle vJ|z^{J}|vJ \rangle$ contains a factor $\gamma \equiv 2B_{e}/\omega_{e}$ to a non-negative power; the conditions that $\gamma \approx 0.0076$ for AlH but smaller for AlD thus ensure that this approximation is valid unless v or J is large.

Discussion

The 19 independently fitted parameters in Table I are the most compact and most physically meaningful representation of all wavenumber data (1201 lines) of vibration-rotational spectra in the ground state $X^{1}\Sigma^{+}$ of AlH in its two characterized isotopic variants $^{27}Al^{1}H$ and $^{27}Al^{2}H$. Because in previous analyses of spectra of AlH not all these data were used, our results are more accurate and are valid over a larger range of energy and (within Born-Oppenheimer separation of electronic and nuclear motions) over a larger range of internuclear distance, than in other work.

Our estimate $g_J = -2.8 \pm 0.5$ based partly on new experimental data²¹ differs somewhat from that, -2.25 ± 0.25 , deduced earlier³³ from fewer and much less precise spectral data. In either case this estimate is the first known derivation of this quantity from only vibration-rotational spectral data of a diatomic moleculeonly wavenumbers of vibration-rotational transitions in the absence of an externally applied magnetic field; for AlH and AlD no pure rotational spectra are available that might enable more precise evaluation of parameters t_i^{H} and u_i^{H} . The only other molecule for which g_J is estimated from such vibration-rotational spectral data is CO₂;⁹ as in that case adiabatic effects were assumed negligible, all the detected effect was attributed to the nonadiabatic rotational contribution—hence to g_{J} . In our work no such assumption is required, because the form of the analytic relations¹⁶ makes clear that adiabatic effects represented explicitly by the coefficient u_1^H can in principle be separately evaluated. Although coefficients u_j^{H} , j > 1, contain contributions from both adiabatic effects and nonadiabatic vibrational effects in unknown proportions, and coefficients $t_j^{\rm H}$, j > 0, likewise contain contributions from both nonadiabatic rotational and vibrational effects, $t_0^{\rm H}$ is associated with purely nonadiabatic rotational effects, hence with the rotational g factor. Measurement of this quantity g_J by means of the Zeeman effect on rotational transitions yields precisely an expectation value $\langle vJ|g_J|vJ\rangle$ within a particular vibrationrotational state. As vibrational and rotational dependences of g_J are relatively small, as discussed above, the value of the rotational g factor of a vibration-rotational state (generally v=0 and J=1) is also nearly the value of g_J.

The sign of g_J for ${}^{27}Al^{1}H$ that we derived from experimental data is negative and its magnitude relatively large, in rough

agreement with the result from our electronic computations. For comparison with molecules having fewer or more numerous electrons, values of g_J for HF and HCl are respectively 0.741 04 and 0.459 35,³⁴ and values of other heteronuclear diatomic hydrides have typically smaller magnitudes and positive signs.¹ Because of both these small magnitudes and the relatively large experimental error in the cases so far tested, we have not previously succeeded to estimate a significant value of g_J from vibrationrotational spectra of diatomic molecules, even for those molecules for which the frequencies of pure rotational lines were measured with precision relatively greater than for wavenumbers of many vibration-rotational transitions of AlH.

The negative sign and relatively large magnitude of our experimentally deduced value of g_J imply, according to eq 14, a paramagnetic contribution, relatively large and independent of temperature, to the total magnetizability. This value agrees satisfactorily with the results of electronic calculations.¹³ Because vibration-rotational spectra provide no information about the diamagnetic contribution thereto, we cannot directly deduce it from only these experimental data. Hence we combine the experimentally deduced paramagnetic contribution with the diamagnetic contribution -6.516 × 10⁻²⁸ J T⁻² according to the CCSDPPA calculation; the total perpendicular component of magnetizability 0.4 × 10⁻²⁸ J T⁻² is thus (marginally) paramagnetic as predicted theoretically.^{13,15}

Work on the magnetizability of several diatomic hydrides having six valence electrons¹³ showed that the paramagnetic contributions in BH and AlH are almost the same because of their similar distributions of electronic density in the valence region, whereas the diamagnetic term in BH is about half that of AlH as a result of the smaller total number of electrons. The experimentally deduced paramagnetism of AlH in the perpendicular component therefore yields the first experimental evidence, albeit indirect, of the paramagnetism, of the van Vleck kind or independent of temperature, of BH in its electronic ground state of class $1\Sigma^+$.

Direct comparison between data in Table II and the radial function $\sum t_j^H z^j$ according to the coefficients t_j^H , $0 \le j \le 3$, in Table I is formally precluded because the latter coefficients t_i^H for j > 0 include unknown contributions from nonadiabatic vibrational effects; the latter are represented by coefficients s_i^{H} that we cannot evaluate at present because experimental data are insufficient for this purpose.¹⁶ In the case of LiH,³⁵ we discovered that the contribution to the term coefficients Z_{kl} in eq 7 from the nonadiabatic vibrational effects was about one quarter of the nonadiabatic rotational effects. For LiH there exist characterized excited electronic states of class ${}^{1}\Sigma^{+}$ with origins at 2.65 \times 10⁶ m^{-1} and ¹II at 3.5 × 10⁶ m⁻¹, whereas for AlH the order of these states is reversed, ${}^{1}\Pi$ at 2.4 × 10⁶ m⁻¹ and ${}^{1}\Sigma^{+}$ at 4.5 × 10⁶ m⁻¹.³⁶ Because according to van Vleck the nonadiabatic vibrational effects formally involve interactions of the ground state Σ^+ with excited states of the same class but nonadiabatic rotational effects with excited states ${}^{1}\Pi, {}^{6}$ we expect that the former effects might be relatively more important for LiH than for AlH because of the relative orders of the electronic origins. In the figure the curve $\Sigma t_i^H z^i$ and the points in Table II are evidently almost parallel, with the differences between the ordinates of thepoints and the curve varying from 0.95 at z = -0.3 to 0.46 at z = +0.2. The difference at z=0 matches closely the difference between $t_0^{\rm H} =$ -2.8 from experimental data and $g_J = -3.37$ from calculations of electronic structure. Whether the deviation between the points and the curve elsewhere reflects the significant influence of the nonadiabatic vibrational effects or merely error propagated through the analysis of existing spectra remains to be ascertained. We fitted the points in Table II to a cubic polynomial in z to generate the relation



Figure 1. Curve of $\Sigma t_j H z^j$ according to values of $t_j H$ from Table I and calculated points of g_j from Table II.

$$g_J = (-3.3115 \pm 0.0096) + (7.22 \pm 0.13)z + (-9.89 \pm 0.53)z^2 + (14.4 \pm 3.3)z^3 (17)$$

in which the stated uncertainties represent a single standard error of coefficients arising from the fitting. The similarity of the values of these coefficients with those denoted t_j^H in Table I is consistent with the deductions from Figure 1 in indicating that most distinction between these two functions $g_J(z)$ and $\Sigma t_j^H z^j$ arises from the discrepancy between the constant terms. As t_0^H is defined poorly from experiment, if the two constant terms proved similar, then the nonadiabatic vibrational effects associated with H in the case of AlH would appear to have smaller magnitudes than the nonadiabatic rotational effects.

Conclusions

The significance of the rotational g factor in the analysis of molecular spectra involving vibration-rotational transitions of multiple isotopic variants of diatomic molecules in the electronic state Σ has been generally understood poorly. If this information, for instance in the form $(0,1|g_1|0,1)$ resulting from microwave spectra with the Zeeman effect, is available from experiments, it should be imposed on the radial functions for the extra rotational effects, such as $\Sigma t_i^{a,b} z^j$ in our eqs 1 and 5, as we have previously done.¹⁶ If no such experimental value is available, one can apply a value calculated according to tested methods of molecular electronic structure as we here describe. If neither information is available, then one can endeavour to evaluate g_J from vibrationrotational spectra of gases accurately measured in the absence of external magnetic fields; tests on simulated spectral data demonstrate that in principle such evaluation is practicable.¹⁶ For this purpose isotopic variants of both nuclei in the diatomic molecule are desirable, but our tests on AlH here reported demonstrate that accuracy and consistency of spectra are extremely important if the value of g_J is to be significantly evaluated.

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