

Radial Functions of $\text{AlH } X^1\Sigma^+$ from Vibration-Rotational Spectra and Spectral Properties of the Group 13 Hydrides

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The coefficients c_j , $j \leq 9$, defining the potential-energy $V(z)$ and coefficients of two other radial functions related to adiabatic and nonadiabatic effects have been determined for AlH in the electronic ground state $X^1\Sigma^+$ by a direct fit to the published frequencies and wavenumbers of vibration-rotational transitions of $^{27}\text{Al}^1\text{H}$ and $^{27}\text{Al}^2\text{H}$. The functions are valid in the range of internuclear distance/ 10^{-10} m [1.24, 2.60]. Some trends in the spectral properties of the group 13 hydrides AlH , GaH , InH and TlH are discussed. The possibility of determining the rotational magnetogyric factor g_j from the available data of only wavenumbers of vibration-rotational transitions is considered; an approximate value $g_j \sim -2.25$ is deduced for $^{27}\text{Al}^1\text{H}$.

INTRODUCTION

Experimental measurements have been made of the vibration-rotational transitions of $^{27}\text{Al}^1\text{H}$ and $^{27}\text{Al}^2\text{H}$, but no pure rotational transitions of either isotopic variant. The measured transitions of AlH in emission consist of lines in the P and R branches of the bands containing the first overtone and others in the sequence $\Delta v = 2$ up to $v' = 8$,¹ as these spectra were measured by means of an interferometer having effectively a broad spectral range, to measure concurrently at a spectral resolution 1.8 m^{-1} all transitions of significant intensity within the range $2400 < \nu/10^2 \text{ m}^{-1} < 3300$ proved practicable. The reported transitions of AlD in absorption include lines in the P and R branches of the fundamental band and others in the sequence $\Delta v = 1$ up to $v' = 7$,² although the effective resolution of the laser diodes operated as sources for these absorption transitions was less than 0.1 m^{-1} , the characteristic performance of these diodes leaves spectral gaps in the wavenumber range within which relatively intense lines are not detectable. For the latter reason only 114 transitions were observed for AlD compared to 333 of AlH despite the fact that the spectral density of lines of AlD exceeds that of AlH .

For few diatomic molecules have vibration-rotational transitions been measured to such large values of the vibrational quantum number as $v = 8$; furthermore the data of the deuteride AlD extend to almost the same value of v as those of the hydride AlH . For these reasons this molecular species provides an opportunity for a useful application of the theory that we have developed to extract the fundamental radial functions directly from the wavenumbers of the spectral transitions. As we have successfully applied this

approach to available spectral data of LiH ,³ SiS ,⁴ LiCl and LiBr ⁵ and to four other metal hydrides AgH , GaH , InH and TlH ,⁶ among several other molecules (unpublished), we are able to make generalisations about chemical trends of the values of the coefficients in the pertinent radial functions that are supposed to represent fundamental molecular properties.⁷ In particular, the molecules AlH , GaH , InH and TlH constitute four of the five possible diatomic hydrides of the group 13 elements; of the remaining hydride BH (and BD), infrared spectra of sufficient quality and quantity are not yet available. Of these elements only Al consists of a single stable isotopic variant ^{27}Al ; for this reason no effect of the finite mass of this nuclide is directly detectable. Even for the elements Ga , In and Tl , each of which has at least two stable nuclides in sufficient natural abundance, no coefficient g_j^{M} or h_j^{M} related to any mass effect of the metallic atom M was determined.⁶ Therefore a comparison of the other sets of corresponding coefficients of these diatomic hydrides MH may provide insight in relation to this family of chemical elements of group 13.

Since the work⁸ of van Vleck and others who extended his treatment, it is known that account of several factors is required to encompass fully the isotopic effects. Elsewhere we have discussed the basis of the application of these theories;⁹ on that basis the sets of wavenumbers of spectral transitions of isotopic variants to available values of quantum number J for rotational angular momentum (in the absence of other contributions to total angular momentum except nuclear spin) may be used to determine accurately not only the potential-energy function but also additional radial functions which describe the other effects, specifically the collective adiabatic and rotational and vibrational nonadiabatic effects that appear to take into ac-

count the approximation inherent in the Born-Oppenheimer separation of electronic and nuclear motions. Such radial functions, having as argument the internuclear distance R or equivalent variable, achieve both the most compact and the most physically meaningful representation of the spectral data.⁷ Here we report the application of this theory to the analysis of the specified spectral data of AlH, with the objective to determine the maximum information about the molecular properties that the data can yield.

PRINCIPLES OF THE METHOD

The salient features of the procedure we recall here as a basis to understand the results of our calculations on AlH. The effective potential energy governing the internuclear vibration and rotation (about the centre of molecular mass) of a diatomic molecule within a particular electronic state of type $^1\Sigma$ contains at most five determinable radial functions and is expressed

$$V_{\text{eff}} = c_0 z^2 \left(1 + \sum_{j=1} c_j z^j \right) + \sum_{j=1} m_e h_j^a z^j / M_a \\ + \sum_{j=1} m_e h_j^b z^j / M_b + B_e J(J+1) \left[1 + \sum_{j=0} m_e g_j^a z^j / M_a \right. \\ \left. + \sum_{j=0} m_e g_j^b z^j / M_b \right] R_e^{-2} / R^2, \quad (1)$$

in which m_e is the electronic rest mass, M_a and M_b are the masses of the separate atoms of types a and b distinguished by their atomic numbers, and the reduced variable z for displacement of internuclear separation R from the equilibrium distance R_e is defined^{10,11}

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

The functions involving the coefficients $h_j^{a,b}$ take empirically into account collectively the adiabatic effects, that the potential energy depends on not only the relative separation of the nuclei but also their momenta, and the non-adiabatic effects related to the vibrational inertia of the electrons, because other effects have different dependences on atomic mass which make them currently negligible with respect to the experimental error of frequency measurements.⁹ The functions involving the coefficients $g_j^{a,b}$ take empirically into account the nonadiabatic effects of the rotational inertia of the electrons, and to some extent also the nonadiabatic effects of the vibrational inertia of the electrons. The two nonadiabatic effects may be considered to arise from interactions between electronic states in-

duced by the vibrational and rotational motions of the nuclei respectively. Defined according to Eq. 1, all coefficients c_j , $g_j^{a,b}$ and $h_j^{a,b}$ are formally independent of mass, and dimensionless (except c_0 and $h_j^{a,b}$). In the case of AlH, because data of Al of only one nuclidic type are available, we need consider no further the effects of variation of its nuclear mass; consequently we specify hereafter g_j^H and h_j^H as the only parameters to treat the features of the spectra of AlH and AlD that depend on mass. As a consequence of the various contributions to the effective potential energy, the vibration-rotational terms consist also of several contributions; the expression for these terms is an extension of Dunham's systematic form,¹²

$$E_{vj} = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl}^{h,H} + Z_{kl}^{g,H}) \\ (v + 1/2)^k (J^2 + J)^l. \quad (3)$$

In this equation in which the explicit isotopic dependence of E_{vj} and the coefficients Y_{kl} and Z_{kl} has been suppressed to simplify the notation, the coefficients Y_{kl} are supposed to result from purely the internuclear potential energy $V(z)$ and the centrifugal motion of the nuclei and associated electrons; the remaining coefficients, the two components of Z_{kl} , reflect respectively the obviously corresponding terms considered as perturbations separately additive in the effective potential energy according to Eq. 1. Analytic expressions of the coefficients Y_{kl} as functions of the harmonic vibrational coefficient k_e (implicitly contained within $U_{1,0}$ or ω_e), the equilibrium separation R_e (implicitly contained within $U_{0,1}$ or B_e), the reduced mass μ and the potential-energy coefficients c_j have been published in machine-readable form complete up to $j = 10$;¹³ further expressions containing coefficients up to $j = 22$ have been generated according to hypervirial perturbation theory.¹⁴ The coefficient c_0 in Eq. 1 is defined in terms either of $U_{1,0}$ and $U_{0,1}$, $c_0 = U_{1,0}^2 / (4U_{0,1})$, or equivalently of k_e and R_e , $c_0 = k_e R_e^2 / (2ch)$; the fundamental physical constants c and h enter these relationships because for spectral applications E_{vj} , Y_{kl} and Z_{kl} are all expressed in wavenumber units. Hence of the five parameters $U_{1,0}$, $U_{0,1}$, c_0 , k_e and R_e , all formally independent of mass, only two are independent; in the actual analysis $U_{1,0}$ and $U_{0,1}$ are determined directly and the others are subsequently derived therefrom. Each term coefficient Y_{kl} and Z_{kl} consists of contributions in series,

$$Y_{kl} = Y_{kl}^{(0)} + Y_{kl}^{(2)} + Y_{kl}^{(4)} + \dots, \quad (4)$$

$$Z_{kl} = Z_{kl}^{(0)} + Z_{kl}^{(2)} + \dots, \quad (5)$$

independently of the method of generation of the actual expressions of the coefficients (or of the notation used to distinguish the contributions). Because the leading contributions $Y_{kl}^{(0)}$ are expressed as a product with the reduced (atomic) mass $\mu = M_a M_b / (M_a + M_b)$,

$$Y_{kl}^{(0)} = U_{kl} \mu^{(1/2 k + 1)}, \quad (6)$$

the coefficients U_{kl} become formally independent of mass. Each auxiliary set of coefficients Z_{kl} is a function of both the potential-energy coefficients c_j and the respective coefficients either g_j^H or h_j^H . The coefficients Y_{kl} depend on the parameters c_j in a highly nonlinear manner, whereas the coefficients Z_{kl} depend on the parameters g_j^H or h_j^H linearly but c_j nonlinearly. A few expressions of Z_{kl}^h in terms of c_j and h_j have been already published in a different but equivalent form,¹⁵ which are however readily converted to be consistent with the present definition according to Eq. 1; a larger collection of expressions containing the coefficients h_j up to $j = 10$ will be published with the extended set of expressions of Y_{kl} . Likewise a few expressions equivalent to Z_{kl}^g in terms of c_j and g_j have been reported;⁹ a larger collection containing g_j up to $j = 10$ will also be published in machine-readable form.

The method of estimation of nonlinear parameters we apply to determine the applicable coefficients c_j , g_j^H and h_j^H directly from the wavenumbers $\tilde{\nu}$ of only the vibration-rotational transitions because for neither AlH nor AlD has a pure rotational transition been measured. The wavenumbers ν of the transitions are the difference of the two terms $E_{v,j}$ of the combining states; the criterion of convergence of a fit to a particular model is that the sum of the squares of the weighted residuals between the measured and calculated values, $\nu_{\text{obs}} - \nu_{\text{calc}}$, is a minimum, hopefully the global minimum (apart from possibly the united atom). The algorithm of the fitting process employs the analytic expressions of not only the term coefficients Y_{kl} and the various components of Z_{kl} but also the first (partial) derivatives of Y_{kl} and the Z_{kl} with respect to the parameters, for instance $\partial Y_{kl} / \partial c_j$, $\partial Y_{kl} / \partial U_{1,0}$ and $\partial Z_{kl} / \partial g_j$. The analytic expressions of the former derivatives up to $j = 10$ have been already published in machine-readable form;¹³ expressions of further derivatives of Y_{kl} and of the derivatives $\partial Z_{kl}^g / \partial g_j$ and $\partial Z_{kl}^h / \partial h_j$ will form part of the large collection to be published subsequently. The various dependences of the residuals on the masses M_H and J make possible the determination of the coefficients g_j^H and h_j^H . Among various models tested during the fitting procedure, involving varied numbers of coefficients in the prospective five functions, we employ the F-value as the criterion of selection; this statistic takes into

account both the number of degrees of freedom (number of data minus the number of fitting parameters) and the standard deviation of the fit. All uncertainties in the tables represent one estimated standard error, and the uncertainties in k_e and R_e take into account also the error in the pertinent fundamental constants.¹⁶ The atomic masses of Al, H and D are from the latest consistent set.¹⁷

RESULTS

The combined data of the vibration-rotational transitions comprised 333 lines of $^{27}\text{Al}^1\text{H}$ and 114 lines of $^{27}\text{Al}^2\text{H}$. To each line was attached an uncertainty, 0.3 m^{-1} for most lines of AlH and 0.08 m^{-1} for most lines of AlD ; other lines not used in the fit of the data of AlH by the original authors¹ (because of relatively small intensity or overlapping of transitions) were assigned uncertainties 3.0 or 30.0 m^{-1} such that their presence in the data set had practically no effect on the values of the resulting parameters. Although all reported lines² of AlD were initially assigned an uncertainty 0.08 m^{-1} , comparable with the standard deviation of fits of analogous data measured in the same laboratory,⁶ attempts to fit the data under these conditions revealed that seven lines had anomalously large residuals; moreover almost all these lines had also relatively large residuals in the spectral reduction by the original authors.² For this reason these seven lines, presumed to constitute errors of measurement, assignment or transcription, were accorded uncertainties increased to 0.8 or 8.0 m^{-1} , such that again these lines exerted no influence on the final values of the parameters. The statistical weight of each data set was set equal to the reciprocal square of the uncertainty of the measured wavenumber. The set of parameters that appear in Table 1 reproduce the observed wavenumbers according to a reduced standard deviation 1.065 ; this value means that on average the data of AlH were reproduced within 0.32 m^{-1} and the data of AlD within 0.085 m^{-1} , with the expectation of those cases of which the uncertainties were set much larger than these values. The numbers compare well with the absolute accuracies claimed by the original authors, "a few" times 0.1 m^{-1} "for the stronger lines" of AlH ¹ and 0.1 m^{-1} for AlD ² respectively.

DISCUSSION

Urban and Jones fitted² the combined data of AlH and AlD by means of twenty parameters of the type U_{kl} and Δ_{kl}^H with a claimed standard deviation 0.80 m^{-1} . The latter

Table 1. Coefficients of the Radial Functions and Other Molecular Properties of $\text{AlH X}^1\Sigma^+$, all Independent of Mass^a

<i>j</i>	<i>c_j</i>	<i>g_j^H</i>	<i>h_j^H/10⁶ m⁻¹</i>
0	(11058139.3 ± 21.1) m ⁻¹
1	-1.280246 ± 0.000025	4.600 ± 0.115	-49.269 ± 0.108
2	0.805224 ± 0.000100	-9.025 ± 0.26	111.36 ± 0.31
3	-0.29014 ± 0.00057		-125.96 ± 0.71
4	0.03935 ± 0.0031		81.1 ± 3.1
5	0.00011 ± 0.0065		
6	-0.3017 ± 0.033		
7	0.2106 ± 0.117		
8	0.627 ± 0.26	<i>U</i> _{1,0} = (165961.055 ± 0.111) m ⁻¹ u ^{1/2} <i>U</i> _{0,1} = (622.68774 ± 0.00202) m ⁻¹ u <i>k_e</i> = (162.27922 ± 0.00024) N m ⁻¹ <i>R_e</i> = (1.6453683 ± 0.0000030) × 10 ⁻¹⁰ m	
9	-1.775 ± 0.64		

^a Each stated uncertainty represents one estimated standard error; the F-value of the fit was 3.75 × 10¹².

statistic would be meaningful only if all (or almost all) the data had the same uncertainty, but in the actual case in which the two sets of data of AlH and AlD have distinctly different uncertainties the reduced standard deviation is a much more reliable measure of the goodness of fit. These values of standard deviation or relative (or 'normalized') standard deviation are sensitive to the values of the relative uncertainties assigned to the data to be fitted; for this reason quantitative comparison of these values between different fits is difficult, but the general magnitudes may still be meaningful. In any case we have used fewer parameters, seventeen instead of twenty, and obtained a better fit; moreover our parameters *c_j*, *g_j^H* and *h_j^H* have in principle the significance of fundamental molecular properties in terms of the radial functions that describe the dependence of the potential energy and other quantities in the context of the Born-Oppenheimer treatment.

Having determined roughly comparable sets of parameters for four hydrides MH of the family of group 13, for which M = Al, Ga, In and Tl, we compare the corresponding values of the more important parameters, according to Table 2. There clearly exist monotonic trends of regular increase or decrease of *c₂*, *c₃*, *h₁^H*, *h₂^H* and *g₁^H*. Although *c₀* varies irregularly for the four compounds, the constituent parameters *k_e* and *R_e* follow definite trends. The rotational coefficient *g₂^H* varies irregularly, within a

Table 2. Comparison of Molecular Parameters of Group 13 Hydrides

Parameter	AlH	GaH	InH	TlH
<i>c₀</i> /m ⁻¹	11058140	10463438	10888492	10095913
- <i>c₁</i>	1.28025	1.34754	1.42967	1.42715
<i>c₂</i>	0.8052	1.0384	1.1315	1.2378
- <i>c₃</i>	0.2901	0.5215	0.5801	0.9948
- <i>h₁^H/10⁶ m⁻¹</i>	49.27	43.92	38.43	33.17
<i>h₂^H/10⁶ m⁻¹</i>	111.4	100.1	91.7	76.5
<i>g₁^H</i>	4.60	4.36	3.83	0.35
- <i>g₂^H</i>	9.03	9.88	8.75	-75.9
<i>k_e</i> /N m ⁻¹	162.3	150.8	128.3	114.6
<i>R_e</i> /10 ⁻¹⁰ m	1.64537	1.66018	1.83598	1.87089

relatively small range, even among the compounds AlH, GaH and InH; the values of both *g₁^H* and *g₂^H* of TlH seem anomalous, but unexpectedly large magnitudes of the parameters *Δ_k* were correspondingly derived in a previous analysis of the spectral data.⁶ As these data of TlH extended¹⁸ to only *v* = 3 perhaps the parameters may not be defined so meaningfully as for other compounds for which the data extended to *v* = 5 at least.

In all these fits to the coefficients *c_j*, *g_j^{M,H}* and *h_j^{M,H}* for the metallic hydrides MH with M = Al, Ga, In and Tl, the values of the coefficients *g₀^{M,H}* were constrained to zero, because an attempted fit of these quantities for LiH previously indicated that they were practically indeterminate from the available data of pure rotational and vibration-rotational transitions, despite the quality and quantity of these data available for the various isotopic variants of LiH.³ When we endeavoured to leave *g₀^H* of AlH as a floating parameter, i.e. free to assume a value during the fit of the available spectral data, we found that a value *g₀^H* ≈ -2.2 appeared to be well determined, i.e. having the relatively small estimated standard error ~0.08. If we identify this value entirely with the contribution to the rotational magnetogyric ratio *g_j* from the H moiety of the molecule AlH, then the equations of Tiemann et al.¹⁹ indicate the corresponding value of *g₀^{Al}* to be slightly smaller in magnitude; the estimate of the latter quantity requires a value²⁰ of the electric dipolar moment *μ_e* ~ 6.7 × 10⁻³¹ C m at the equilibrium separation *R_e*, taken from a theoretical calculation because no experimental value is known. When we take all this information into account, we propose that according to the available data and theoretical formulation the best estimates of the various pertinent parameters are *g₀^H* ~ -2.15 ± 0.10, *g₀^{Al}* ~ -2.10 ± 0.10 and for ²⁷Al¹H *g_j* ~ -2.25 ± 0.25; the relatively large uncertainty attached to the latter quantity takes into account the fact that, although the estimated standard deviation of *g₀^H* was found relatively small in the fitting procedure according to which its value was deduced,

the magnitudes of the correlation coefficients connecting g_0^H with other parameters were relatively large. Moreover there remains at present some uncertainty whether the only or dominant contribution to $g_0^{a,b}$ is the molecular magnetogyric ratio g_I . As the latter quantity reflects rotational nonadiabatic effects, its theoretical computation is difficult, and no estimates are known for comparison with the proposed value here deduced. Because no stable isotopic variant of Al is available, the spectral data are completely insensitive to the value of g_0^{Al} . When the coefficient g_0^H was admitted into the parameter set, i.e. when it was permitted to assume a value other than zero either constrained near -2.2 or freely floated, some other parameters in Table 1 altered appreciably; specifically, not only the magnitudes of the coefficients h_j^H increased significantly but also the values of their estimated standard errors increased, although the relative standard deviation of the fit that included only eighteen floated parameters increased only marginally to 1.11. Such an effect on the coefficients h_j^H we expect because of the close relationships within the equations describing the adiabatic and nonadiabatic effects. These circumstances indicate that the inclusion of the parameters $g_0^{Al,H}$ is probably physically meaningful. When the theory of these adiabatic and nonadiabatic effects is extended, a reexamination of the spectral data of AlH and AlD is warranted. Because the set of parameters lacking $g_0^{Al,H}$ yielded a slightly better fit of the spectra than any set including the latter coefficients, the values in Table 1 are at present preferred to yield the best reproduction of the spectral data.

CONCLUSION

Directly from the wavenumbers of the vibration-rotational transitions of AlH and AlD in the electronic ground state $X^1\Sigma^+$, we have determined the coefficients (Table 1) of three radial functions which are independent of mass and compared them (Table 2) with corresponding coefficients of other diatomic hydrides of the group 13 metals. The range/ 10^{-10} m, approximately [1.24, 2.60], of validity of these functions of AlH corresponds to roughly the classical turning points of the state $v = 8$ of $^{27}\text{Al}^1\text{H}$, the vibrational state of greatest energy in the available transitions. These functions may serve as tests of the accuracy of quantum computations on this relatively simple molecular species. We have estimated a value $g_I = -2.2$ of the rotational magnetogyric factor of $^{27}\text{Al}^1\text{H}$ from the wavenumber data of

vibration-rotational transitions.

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Key Words

Vibration-rotational analysis; Fundamental radial functions; Potential energy.

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