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Electric and magnetic molecular properties from analysis of vibration–rotational spectral data of samples measured without applied fields – application to GaH X $^1\Sigma^+$

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Abstract

In total 1094 lines of vibration–rotational transitions of ^{69}Ga^{1}H, ^{71}Ga^{1}H, ^{69}Ga^{2}H and ^{71}Ga^{2}H were analyzed to yield the coefficients of radial functions to represent the internuclear potential energy and the adiabatic and nonadiabatic rotational and vibrational effects of the nuclei. From the parameters $t_0^{\mathrm{Ga,H}}$ that reflect purely the nonadiabatic rotational effects, we show how to estimate the molecular rotational g factor and the electric dipole moment from spectra of samples without the application of electric and magnetic fields; we apply this method to deduce $g_J = -3.22 \pm 0.1$ for ^{69}Ga^{1}H and elicit information about the magnetic susceptibility of GaH. The maximum range of validity of radial functions of GaH X $^1\Sigma^+$ is $1.31 \leqslant R/10^{-10}\,\mathrm{m} \leqslant 2.36$.

1. Introduction

Current measurements of infrared spectra are so precise as to present a challenge to development of quantitative theoretical bases of their treatment. For instance, for spectra of GaH measured in emission [1], both absolute accuracy and precision are claimed to attain ≈ 0.01 m^{-1} for many lines that extend into the region near 160000 m^{-1}; even though this relative precision is $\approx 6 \times 10^{-8}$, it proved practicable, by means of 29–70 parameters (in various sets), to reproduce these lines, among others in a collection numbering more than a thousand [1]. The parameters in these sets were empirically based but a theoretical basis exists according to which we applied a model that conveys both physical and chemical significance [2]. Our theory originated in Van Vleck's delineation of adiabatic effects, whereby internuclear potential energy depends on not only the distance between the nuclei but also their relative momenta, and nonadiabatic rotational and vibrational effects, whereby the electrons fail to follow perfectly the associated nuclei in their respective rotational and vibrational motions [3]. The imposition of the classical notion of molecular structure onto a formally quantum-mechanical (quantal) system allows us to treat the various effects in terms of radial functions, i.e. functions of internuclear distance R. Although these functions are not quantal observables, they are well defined according to known methods of quantum-chemical calculations; hence by separation of electronic and nuclear motions according to the procedure of Born and Oppenheimer [4], one can directly or indirectly calculate these radial functions. The evaluation of segments of these functions from experimental data, mainly from precise spectral measurements, involves a process of inversion that has never been proved unique [5]. Despite this hin-

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drance to interpretation associated classically with rotational and vibrational motions of the nuclei and associated electrons, there is convenience in being able to reduce numerous spectral measurements, specifically the wavenumbers of transitions in the infrared spectrum, to relatively few parameters by means of which one can reproduce accurately the measurements and which one can relate to the results of quantal computations. Moreover the radial functions appear to convey physical and chemical significance within a classical context, despite their being artifacts superfluous to a truly quantal formalism [6].

Here we present an analysis of all available infrared spectra of GaH in its several isotopic variants to evaluate the parameters in pertinent radial functions. Although during the spectral measurements the gaseous samples were confined to a region essentially free of electric and magnetic fields, we derived information about magnetic properties of this species from only the wavenumbers of spectral lines and atomic masses. Even if we claim this information to be evaluated not highly accurately, because of finite accuracy of spectral measurements, in the absence of other, more direct, experimental measurement of this magnetic property we proffer this result as the first indication of such a value from experiment.

2. Treatment of experimental data and results

Our procedure is based on a theoretical formalism [2] and its implementation in a tested algorithm [7]. We review here the salient features of the procedure to extract the molecular properties of interest.

In an effective Hamiltonian for nuclear motion of the form [2]

$$\begin{aligned}\mathscr{H}_{\mathrm{eff}} &= \hat{P}[1+\beta(R)]\hat{P}/2\mu + V(R) + V'(R)\\ &\quad + hcB_{\mathrm{e}}[1+\alpha(R)]J(J+1)R_{\mathrm{e}}^2/R^2\,, \qquad (1)\end{aligned}$$

R_e is the equilibrium internuclear separation and $\hat{P}$ the operator for the linear momentum of the nuclei; other quantities are defined below. To apply these functions we transform to the reduced displacement variable

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

that possesses the property of remaining finite throughout the range of molecular existence: for $0 \leqslant R < \infty$, $-2 \leqslant z < 2$ [8,9]. With SI units of wavenumber [10] the potential energy $V(R)$ independent of nuclear mass we represent in the form

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

For a diatomic molecule AB having nuclei of unlike protonic numbers and reduced mass μ, the remaining functions dependent on individual nuclear masses M_a and M_b we represent by means of separate expansions for the nucleus of each type A and B; we have for the nonadiabatic vibrational effects,

$$\beta(R) \to m_{\mathrm{e}}\left(\sum_{j=0} \frac{s_j^{\mathrm{a}} z^j}{M_{\mathrm{a}}} + \sum_{j=0} \frac{s_j^{\mathrm{b}} z^j}{M_{\mathrm{b}}}\right) \qquad (4)$$

for the nonadiabatic rotational effects,

$$\alpha(R) \to m_{\mathrm{e}}\left(\sum_{j=0} \frac{t_j^{\mathrm{a}} z^j}{M_{\mathrm{a}}} + \sum_{j=0} \frac{t_j^{\mathrm{b}} z^j}{M_{\mathrm{b}}}\right) \qquad (5)$$

and for the adiabatic effects (combined with any residual nonadiabatic vibrational effects [2]),

$$V'(R) \to m_{\mathrm{e}}\left(\sum_{j=1} \frac{u_j^{\mathrm{a}} z^j}{M_{\mathrm{a}}} + \sum_{j=1} \frac{u_j^{\mathrm{b}} z^j}{M_{\mathrm{b}}}\right). \qquad (6)$$

Then the molecular energies within a particular electronic state, or vibration–rotational terms, we express in the form [7]

$$\begin{aligned}E_{vJ} &= \sum_{k=0}\sum_{l=0} \left(Y_{kl} + Z_{kl}^{\mathrm{r,a}} + Z_{kl}^{\mathrm{r,b}} + Z_{kl}^{\mathrm{v,a}} + Z_{kl}^{\mathrm{v,b}}\right)\\ &\quad \times (v+\tfrac{1}{2})^k (J^2+J)^l \qquad (7)\end{aligned}$$

in which the dependence of the various term coefficients Y_{kl} and Z_{kl} on the radial coefficients is explained elsewhere [7].

The available infrared spectral data of GaH of usable quality result from absorption by ^{69}Ga^{1}H and ^{71}Ga^{1}H together [11], and of ^{69}Ga^{2}H and ^{71}Ga^{2}H together [12], and from emission of these species [1]. Because characteristics of the laser [11,12] precluded continuous tuning over the broad ranges, many lines in each band were immeasurable; for this reason only 113 lines of GaH, almost evenly divided between species ^{69}Ga^{1}H and ^{71}Ga^{1}H, and analogously 95 lines of GaD, for $\Delta v = 1$ up to $v' = 5$ and $J \leqslant 29$ in P and R branches were reported. Spectra transformed from interferograms included 147 lines of

^{69}Ga^{1}H, 143 lines of ^{71}Ga^{1}H, in both cases up to $v'=4$ and $J'=29$, 393 lines of ^{69}Ga^{2}H and 362 lines of ^{71}Ga^{2}H, in both cases up to $v'=7$ and $J'=48$, 1045 transitions in total. Because all later measurements [1] on GaD and some on GaH duplicated previous measurements [11,12] but at generally greater precision, we added only 49 lines [11] of GaH to 1045 lines [1] to comprise our input data set. Before adding these lines we verified by means of duplicated lines that no discernible systematic shift of wavenumbers exists between measurements made with the diode laser [11,12] and the interferometer [1].

Of various models (sets of parameters) tested during the fitting process according to the criterion of the maximum F statistic [7], the results of the best fit in Table 1 constitute the parameters, each with its estimated (single) standard error, in the set evaluated from specified spectral data of all isotopic variants of GaH. For comparison with results from other sources our programme generates secondarily values of U_{kl} and $\Delta_{kl}^{\mathrm{a,b}}$ in a commonly applied empirical relation [13]

$$E_{vJ}=\sum_{k=0}\sum_{l=0}U_{kl}\mu^{-(\frac{1}{2}k+l)}(v+\tfrac{1}{2})^k[J(J+1)]^l$$
$$\times[1+m_\mathrm{e}(\Delta_{kl}^\mathrm{a}/M_\mathrm{a}+\Delta_{kl}^\mathrm{b}/M_\mathrm{b})] \qquad (8)$$

for which our work [2] provides a systematic theoretical justification. Our values of Δ_{kl}^a are derived directly from the sum of term coefficients $Z_{kl}^{\mathrm{v,a}}+Z_{kl}^{\mathrm{r,a}}$, and analogously for Δ_{kl}^b, whereas all purely *mechanical* effects are taken into account in the principal term coefficients Y_{kl} in Eq. (7) that include all pertinent contributions of whatever order. In contrast, values of $\Delta_{kl}^{\mathrm{a,b}}$ generally reported (e.g. in Ref. [1] or Ref. [12]) include implicitly contributions to Y_{kl} of order greater than that of $U_{kl}\equiv Y_{kl}^{(0)}\mu^{(\frac{1}{2}k+1)}$; hence values of $\Delta_{kl}^{\mathrm{a,b}}$ from other sources reflect not only adiabatic and nonadiabatic effects but also mechanical effects in $Y_{kl}^{(2)}$. Because of their secondary generation in the programme Radiatom based on various nonlinear combinations of the primary parameters that are coefficients in the radial functions, most values of U_{kl} and $\Delta_{kl}^{\mathrm{Ga,H}}$ in Table 2 lack associated standard errors, in common with most values of U_{kl} previously reported [1].

3. Discussion

By means of 23 independently adjustable parameters in Table 1 we reproduced the wavenumbers of 1094 transitions of four isotopic variants of GaH within the best estimates of uncertainties of their measurements. When we used the parameter set of

Table 1

Coefficients of the radial functions and other molecular properties of GaH X $^1\Sigma^+$, all independent of mass [a]

j	c_j	t_j^H	u_j^Ga (10^6 m^{-1})	u_j^H (10^6 m^{-1})
0	(10463044.4±22.0) m^{-1}	−3.17061±0.00064		
1	−1.34751214±0.0000124	7.3734±0.0191	[0]	−10.80911±0.00105
2	1.038606±0.000054	−15.131±0.27	5.515±0.83	[0]
3	−0.522339±0.000164	16.294±0.42	38.89±13.8	30.812±0.91
4	0.045332±0.00059			−71.31±4.0
5	−0.11843±0.0026			141.6±11.5
6	0.25625±0.0071			−256.8±28.4
7	−0.0462±0.032			
8	−1.632±0.106			

$t_0^\mathrm{Ga}=-3.72\pm0.34$
$t_1^\mathrm{Ga}=3.545\pm0.71$

$U_{1,0}/\mathrm{m}^{-1}\,u^{1/2}=159996.295\pm0.052$
$U_{0,1}/\mathrm{m}^{-1}\,u=611.64833\pm0.00169$
$k_\mathrm{e}/\mathrm{N\,m}^{-1}=150.823976\pm0.000133$
$R_\mathrm{e}/10^{-10}\,\mathrm{m}=1.6601502\pm0.0000027$
range of validity is $1.31\leqslant R/10^{-10}\,\mathrm{m}\leqslant2.36$

[a] Each stated uncertainty represents one estimated standard error; the normalised standard deviation of the fit of 1094 data was 0.92; the F value was 3.3×10^{15}. Values of parameters enclosed by brackets and all $s_j^{\mathrm{Ga,H}}$ were constrained to zero during fitting.

Table 2
Auxiliary parameters U_{kl}, Δ_{kl}^{Ga} and Δ_{kl}^{H} of GaH [a]

$k\ l$	This work	$U_{kl}/\mathrm{m}^{-1}\ u^{1/2k+l}$	
		Ref. [1]	Ref. [11]
1 0	159996.295±0.052	159996.201±0.060	159998.32±0.17
2 0	−2824.5709	−2824.5050±0.0183	−2826.169±0.079
3 0	31.8640	31.8364±0.0084	33.397±0.019
4 0	−0.60282	−0.59808±0.00170	−0.6825±0.0016
5 0	−0.004211	−0.004574±0.000124	–
0 1	611.648325±0.00169	611.63629±0.00139	611.6337±0.0045
1 1	−18.905044	−18.904727±0.000046	−18.991805±0.00078
2 1	0.271677	0.271818±0.000028	0.28141±0.00018
3 1 /10^{-3}	−4.3784	−4.4162±0.0085	6.404±0.17
4 1 /10^{-4}	−1.3379	−1.2901±0.0099	–
0 2 /10^{-2}	−3.5756	−3.5754	−3.5725±0.0010
1 2 /10^{-3}	0.8482	0.8483	0.8676±0.019
2 2 /10^{-5}	−0.7570	−0.7747	−1.798±0.015
3 2 /10^{-5}	−0.1154	−0.1101	–
4 2 /10^{-8}	0.5682	−0.0563	–
0 3 /10^{-5}	0.13638	0.13636	0.12414±0.00042
1 3 /10^{-7}	−0.1268	−0.1263	−0.234±0.015
2 3 /10^{-8}	−0.2986	−0.2976	–
3 3 /10^{-10}	0.6107	0.4976	–
0 4 /10^{-10}	−0.5643	−0.5641	–
1 4 /10^{-11}	−0.1385	−0.1446	–
2 4 /10^{-13}	−0.8607	−0.5534	–
3 4 /10^{-13}	−0.2152	−0.2420	–
0 5 /10^{-14}	0.3353	0.3353	–
1 5 /10^{-15}	−0.2377	−0.2279	–
2 5 /10^{-16}	0.2483	0.1464	–
0 6 /10^{-18}	−0.2489	−0.2507	–
1 6 /10^{-20}	0.5120	0.7527	–
2 6 /10^{-20}	−1.0055	−0.8987	–
0 7 /10^{-22}	0.1017	0.1046	–
1 7 /10^{-23}	0.1170	0.0115	–
0 8 /10^{-27}	−0.7849	−0.7632	–
1 8 /10^{-27}	−0.7171	−0.5574	–
0 9 /10^{-31}	0.6795	0.5509	–
0 10 /10^{-34}	−0.1106	0.0905	–

$k\ l$	This work	Δ_{kl}^{Ga}	
		Ref. [1]	Ref. [11]
1 0	0.264	0.238±0.046	–
0 1	−3.721	−1.08±0.26	–
1 1	−3.549	–	–
0 2	−11.515	–	–
0 3	5.73	–	–

Table 2
Continued

$k\,l$	This work	Δ^{H}_{kl}	
		Ref. [1]	Ref. [11]
1 0	−1.56060	−1.62023±0.00026	−1.6168±0.0017
2 0	−2.1198	−1.9838±0.0076	−1.913±0.018
3 0	−1.355	−1.216±0.105	–
0 1	−4.20368	−4.21839±0.00077	−4.251±0.016
1 1	−3.2939	−3.1193±0.0055	−2.901±0.045
2 1	−0.847	−0.629±0.085	–
0 2	−13.692	−13.297±0.020	−14.55±0.52
1 2	−7.825	−6.671±0.81	–
2 2	8.95	–	–
0 3	−50.89	−36.93±0.27	–
1 3	−71.89	–	–
0 4	−132.41	–	–
1 4	146.16	–	–
0 5	30.66	–	–
0 6	54.06	–	–

[a] The notation – signifies that this parameter was not evaluated.

Campbell et al. [1], we discovered small but systematic discrepancies in the reproduction of the 4–3 bands of $^{69}Ga^{1}H$ and $^{71}Ga^{1}H$; predictions of lines of bands 5–4 indicated larger negative deviations of the calculated wavenumbers of the same isotopic species, even though the energy of the vibrational state $v=5$ of GaH is comparable with those of $v=6$ and 7 of GaD. Inclusion of lines of 5–4 bands [11] into our data set yielded a fit of satisfactory quality with neither discernible systematic discrepancies nor trends. According to this criterion our parameters of radial functions in Table 1 have satisfactory statistical significance. Values of parameters not stated to have finite magnitudes in Table 1 were constrained to zero during the fitting process; such parameters include all $s_j^{\mathrm{Ga,H}}$ because available data are insufficient to allow their separate evaluation, as explained elsewhere [7]. Specifically, the values of parameters $u_j^{\mathrm{Ga,H}}$ with $j>1$ or t_j^{H} with $j>0$ incorporate not only their nominal adiabatic or nonadiabatic rotational effects, respectively, but also the nonadiabatic vibrational effects of the inestimable parameters $s_j^{\mathrm{Ga,H}}$ that are included within the same term coefficients $Z_{kl}^{\mathrm{v,Ga}}$ and $Z_{kl}^{\mathrm{v,H}}$, or $Z_{kl}^{\mathrm{r,Ga}}$ and $Z_{kl}^{\mathrm{r,H}}$ respectively [2,7]. Values of potential-energy coefficients c_j, $0\leqslant j\leqslant 8$, in Table 1 are similar to those in our previous analysis [14] of 208 transitions of GaH and GaD [11,12], but the improved precision of our present results reflects the more extensive and more precise data in our input set of transitions; the maximum range of validity, $1.31\leqslant R/10^{-10}\ \mathrm{m}\leqslant 2.36$, of the present radial functions is the same as previously [14] because the spectral data [1] lie within the range of previous data [11,12].

In preliminary fits of the data, we discovered that correlation coefficients linking t_0^{Ga} and u_1^{Ga} and linking t_0^{H} and u_2^{H} had large magnitudes; furthermore the value of u_1^{Ga} had a relatively small magnitude and large error, whereas the value of t_0^{Ga} was zero within moderate error. When in further fits with varied sets of parameters tested with the F statistic [7] we constrained both u_1^{Ga} and u_2^{H} to zero, the values of both t_0^{Ga} and t_0^{H} decreased to less than −3 and the standard errors of not only both these and several other parameters but also the number of entries in the parameter correlation matrix with magnitudes greater than 0.9 decreased markedly. For instance the relative error of t_0^{H} is 0.002 and that of u_1^{H} is 0.0001. All these conditions indicate a statistically acceptable fit of 1094 data to 23 independently adjustable and meaningful parameters.

Comparison in Table 2 of the values of coefficients U_{kl} and $\Delta_{kl}^{\mathrm{Ga,H}}$ between the present indirect fits to these parameters and the previous direct fits [1,12] exhibits strong similarities between values belonging to these two sets, although generally the differences between corresponding coefficients exceed a few standard errors (where specified). Apart from the varied number of parameters in each set, one reason for this variation is that our values of $\Delta_{kl}^{\mathrm{Ga,H}}$ contain no purely mechanical contribution, only the adiabatic and nonadiabatic effects; moreover the data sets were distinct and our coefficients produce no systematic deviations. Although for $^1H^{35}Cl$ [7] the magnitudes of contributions to vibration-rotational energies from some $Y_{kl}^{(2)}$ were comparable with those of Z_{kl}^{H}, for $^{69}Ga^1H$ or $^{71}Ga^1H$ generally the contributions are relatively less important.

We list in Table 2 values (for comparison with the 35 values reported [1]) of coefficients U_{kl}; the existence with significant magnitudes of values of R_e and c_j, $0 \leqslant j \leqslant 8$, implies the existence of precisely these 35 non-zero values of U_{kl} with $2k+l \leqslant 10$. Clearly the reduction of numerous spectral data to R_e and these nine coefficients c_j, $0 \leqslant j \leqslant 8$, of the potential-energy function is more economical than the alternative representation in terms of the constrained values of the term coefficients U_{kl}, and also more economical than the 19 unconstrained values of U_{kl} [1]; such fitting of spectral data by means of unconstrained values lacks theoretical justification [15,16]. The parameters in sets $t_j^{\mathrm{Ga,H}}$ and $u_j^{\mathrm{Ga,H}}$ that number 13 in Table 1 likewise yield a more compact representation of adiabatic and nonadiabatic effects than the corresponding sets of 20 values (Table 2) of $\Delta_{kl}^{\mathrm{Ga,H}}$ implied by the former parameters in the same way that ten values of R_e and c_j, $0 \leqslant j \leqslant 8$, imply 35 values of term coefficients U_{kl} according to Eq. (8). Only eleven freely fitted values of $\Delta_{kl}^{\mathrm{Ga,H}}$ were employed in the previous fit of 1045 spectral lines [1], and only five values in the fit of 208 other lines [11], but values in those sets proved inadequate to reproduce all spectral data without systematic discrepancies, as explained above. In our comparison of values from various sources in Table 2, some values of corresponding parameters are similar, such as $U_{1,0}$, agreeing within two estimated standard errors. Whether values of $\Delta_{kl}^{\mathrm{Ga,H}}$ would so agree if other sets of parameters represented more satisfactorily all available spectral data would depend on the tendency of mechanical contributions to $\Delta_{kl}^{\mathrm{Ga,H}}$ to be relatively small or to cancel. Our parameters in Table 2 used (with applicable values of $Y^{(2)}$ and $Y^{(4)}$ implied [17] by coefficients c_j in Table 1) as a set of consistent with respect to Eq. (8) reproduce the data better than previously reported parameters [1,12].

Our results feature values of $t_0^{\mathrm{Ga,H}}$; from the free fit $t_0^{\mathrm{Ga}} = -3.72 \pm 0.34$ and $t_0^{\mathrm{H}} = -3.1706 \pm 0.00064$. If these standard errors reflect accurately the true uncertainties of these parameters, both t_0^{Ga} and t_0^{H} are well defined. Tests on simulated spectral data [7], which lacked the equivalent of measurement error other than rounding of values at $0.0001\ \mathrm{m}^{-1}$, proved these parameters to be reproduced satisfactorily, without significant correlation, under those conditions [7]. In less than ideal conditions inevitably encountered in measurements, accurate evaluation of these parameters is problematic. For lack of other results we made use of these values of both t_0^{Ga} and t_0^{H}, as explained below. Of the radial coefficients only c_7 appears poorly significant, but in this case the fortuitously small magnitude of c_7 makes the ratio $\delta c_7 / |c_7|$ with the estimated standard error anomalously large. The value of c_8 is absolutely required to fit data of GaH up to $v=5$ and GaD up to $v=7$, and the nonlinear relationship between term coefficients Y_{kl} and these potential-energy parameters makes it impracticable to include c_8 without c_7.

As there exist radial functions of three kinds apart from potential energy, namely $\alpha(R)$, $\beta(R)$ and $V'(R)$, to be defined but information from only two sources, namely the variation of isotopic masses of nuclei of each type A or B and the extra rotational dependence, it is in general impracticable to evaluate separately adiabatic and nonadiabatic rotational and vibrational effects from only spectral data of samples without applied external fields, as previously discussed [7]. Because of the way that term coefficients Z_{kl}^{r} and Z_{kl}^{v} depend on parameters in these three radial functions, apart from potential energy that is separately evaluated from the term coefficients Y_{kl}, coefficients u_1^{Ga} and u_1^{H} formally represent purely adiabatic effects and coefficients t_0^{Ga} and t_0^{H} formally represent purely nonadiabatic rotational effects. The remaining coefficients of each type include within them not only nominal adiabatic effects in u_j, $j > 1$, and nonadiabatic rotational effects in t_j, $j > 0$, but also in both cases nonadiabatic vibrational effects nominally taken into account in s_j, $j \geqslant 0$; these effects are inextricably intertwined under present conditions. Hence we interpret u_1^{Ga} having a negligible magnitude to signify that adiabatic effects are small for the relatively massive nuclei ^{69}Ga and ^{71}Ga, consistent with the negligible values for both Si and S in SiS for which values of $t_0^{\rm Si,S}$ were imposed on the basis of other spectral information (g_J and μ_e, vide infra) [18]. For $u_2^{\rm H}$ also to be negligible there is no obvious explanation, but one can readily see that both $u_1^{\rm H}$ and $u_3^{\rm H}$ have relatively large magnitudes but opposite signs; the shape of the effective radial function $\Sigma\, u_j^{\rm H} z^j$ evidently requires a value of $u_2^{\rm H}$ near zero.

Although all these adiabatic and nonadiabatic effects are formally artifacts arising from separate treatment of electronic and nuclear motions [4], nonadiabatic rotational effects in particular are related to a property directly measurable in an experiment, namely the rotational g factor; the product of this quantity g_J and the nuclear magneton μ_n is the magnetogyric ratio, the ratio of magnetic dipole moment to rotational angular momentum. As a useful approximation, measuring by means of the Zeeman effect the expectation value $\langle vJ|g_J|vJ\rangle$ in states of small values of v and J, commonly $\langle |0,1|g_J|0,1\rangle$, yields g_0, the constant term in a polynomial expansion of the operator g_J in an appropriate representation; the leading rotational and vibrational dependences of $\langle vJ|g_J|vJ\rangle$ would yield coefficients of respectively linear and quadratic terms in such a series [19]. According to relations [20] for a dipolar molecule AB of relative polarity $^+$AB$^-$, the quantity g_0 we apportion to separate nuclei as

$$t_0^{\rm a} \approx \mu[g_0/m_{\rm p} + 2\mu_e/(eR_eM_{\rm b})]\,, \qquad (9)$$

$$t_0^{\rm b} \approx \mu[g_0/m_{\rm p} - 2\mu_e/(eR_eM_{\rm a})]\,, \qquad (10)$$

in which μ is the reduced mass of a particular isotopic variant, $m_{\rm p}$ is the protonic rest mass, e is the protonic charge, and μ_e is the electric dipole moment at equilibrium separation R_e. In terms of unknown quantities g_0 and μ_e, Eqs. (9) and (10) become

$$\mu_e \approx \tfrac{1}{2}eR_e(t_0^{\rm a} - t_0^{\rm b})\,, \qquad (11)$$

$$g_0 \approx m_{\rm p}(t_0^{\rm a}/M_{\rm a} + t_0^{\rm b}/M_{\rm b})\,. \qquad (12)$$

Applying these relations to our estimates in Table 1 of $t_0^{\rm Ga,H}$ of assumed polarity $^+$GaH$^-$, we estimated the unknown quantities g_0 and μ_e, hence $g_0 \approx -3.223 \pm 0.011$ for ^{69}Ga^{1}H that we identify with the rotational g factor, and $|\mu_e| \approx (7.3 \pm 4.7) \times 10^{-30}$ C m to signify the electric dipole moment of GaH. The value of g_0 has a large magnitude, relative to HF, HCl, DBr and DI that are in the range [0.10, 0.45] [21], but a negative sign. An even larger magnitude -8.3 and negative sign of g_J for the isovalent molecule BH [22] are associated with the predicted net paramagnetic susceptibility of this species [23]. The same term [21] that with a positive sign contributes to paramagnetic susceptibility occurs with a negative sign in the expression for the rotational g factor. We lack a method to deduce information about the diamagnetic contribution to the total susceptibility from spectral data of GaH. As neither measurement nor calculation of either g_J or magnetic susceptibility of GaH is published for comparison, we present the estimate $g_J \approx -3.2 \pm 0.1$ of ^{69}Ga^{1}H as a prediction; the increased uncertainty takes into account potential ambiguities resulting from the nature of the parameter set.

For the electric dipole moment of GaH, our magnitude $(7.3 \pm 4.7) \times 10^{-30}$ C m much exceeds results of two calculations [24,25], both about 1.2×10^{-30} C m and lacking any estimate of error, but the large error associated with our estimate of μ_e obviously limits its validity. According to Eq. (11), in order to produce such a relatively small value as the latter, values of $t_0^{\rm a}$ and $t_0^{\rm b}$ must have the same sign and similar magnitudes; the value $t_0^{\rm Ga} = -3.08$ necessary to produce such a small magnitude of the dipole moment differs from the calculated value by less than two estimated standard errors. Because $t_0^{\rm Ga}$ is poorly defined, Eq. (11) for μ_e that implies a small difference between two relatively large values is less reliable than Eq. (12); the reason is that, because the atomic mass of Ga exceeds so much that of H, the value of g_J from Eq. (12) is insensitive to the value of $t_0^{\rm Ga}$ unless either the magnitudes of $t_0^{\rm H}$ and $t_0^{\rm Ga}$ are comparable as in the present case, or the magnitude of $t_0^{\rm Ga}$ is much less than that of $t_0^{\rm H}$. Because of the relatively small fractional alteration of mass between ^{69}Ga and ^{71}Ga, $t_0^{\rm Ga}$ is more difficult to evaluate from data than $t_0^{\rm H}$. The finite accuracy of experimental data ultimately limits the accuracy of $t_0^{\rm Ga}$ and $t_0^{\rm H}$, because tests on simulated spectral data proved that under nearly ideal conditions comparable values of $t_0^{\rm a}$ and $t_0^{\rm b}$ are accurately reproduced [7]. Precise measurements of pure rotational transitions of all four isotopic species of GaH in the sub-millimetre region, for instance by interferometric methods in connection with which Stark and Zeeman techniques are difficult to apply, would likely improve the precision and reliability of electric and magnetic properties estimated according to our new approach.

4. Conclusion

Numerous spectral data of isotopic variants of GaH, namely all known wavenumbers of their vibration–rotational transitions, we reduced to parameters of radial functions that are relatively few (only 23, compared with 29 [1]), which we demonstrate to provide both a compact and a physically and chemically meaningful representation of these data. We deduced information about magnetic properties of a molecule from only wavenumbers of vibration–rotational transitions measured in the absence of external electric and magnetic fields. We explain how to estimate both the rotational g factor and the electric dipole moment of a diatomic molecule from such spectral data; hence we predicted the value $g_J \approx -3.2$ of ^{69}Ga^{1}H.

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References

[1] J.M. Campbell, M. Dulick, D. Klapstein, J.B. White and P.F. Bernath, J. Chem. Phys. 99 (1993) 8379.
[2] F.M. Fernandez and J.F. Ogilvie, Chin. J. Phys. 30 (1992) 177, 599, and references therein.
[3] J.H. Van Vleck, J. Chem. Phys. 4 (1936) 327.
[4] M. Born and J.R Oppenheimer, Ann. Phys. 84 (1927) 457.
[5] R. Engelke, Am. J. Phys. 57 (1989) 339.
[6] L. Lathouwers and P. van Leuven, Advan. Chem. Phys. 49 (1982) 115.
[7] J.F. Ogilvie, J. Phys. B. 27 (1994) 47.
[8] J.F. Ogilvie, Proc. Roy. Soc. London A 378 (1981) 287; A 381 (1982) 479.
[9] J.F. Ogilvie, J. Chem. Phys. 88 (1988) 2804.
[10] E.R. Cohen and P. Giacomo, Physica A 146 (1987) 1.
[11] R.D. Urban, U. Magg and H. Jones, Chem. Phys. Letters 154 (1989) 135.
[12] R.D. Urban, H. Birk, P. Polomsky and H. Jones, J. Chem. Phys. 94 (1991) 2523.
[13] A.H.M. Ross, R.S. Eng and H. Kildal, Opt. Commun. 12 (1974) 433.
[14] J.F. Ogilvie, Chem. Phys. Letters 191 (1992) 592.
[15] J.K.G. Watson, J. Mol. Spectry. 80 (1980) 411.
[16] V.G. Tyuterev and T.I. Velichko, Chem. Phys. Letters 104 (1984) 596.
[17] J.F. Ogilvie, Comput. Phys. Commun. 30 (1983) 101.
[18] J.F. Ogilvie and S.-C. Liao, Acta Phys. Hung., to be published.
[19] R.H. Tipping and J.F. Ogilvie, J. Mol. Struct. 35 (1976) 1.
[20] E. Tiemann, W.U. Stieda, T. Torring and J. Hoeft, Z. Naturforsch. 30a (1975) 1606.
[21] W. Gordy and R.L. Cook, Microwave molecular spectra, 3rd Ed. (Wiley, New York, 1984), and references therein.
[22] S.P.A. Sauer, J. Oddershede and J. Geertsen, Mol. Phys. 76 (1992) 445.
[23] R.M. Stevens, R.M. Pitzer and W.N. Lipscomb, J. Chem. Phys. 38 (1963) 550.
[24] L.G.M. Pettersson and S.R. Langhoff, J. Chem. Phys. 85 (1986) 3130.
[25] P. Schwerdtfeger, G.A. Heath, M. Dolg and M.A. Bennett, J. Am. Chem. Soc. 114 (1992) 7518.