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The electric polarity +GeS⁻ from analysis of only frequencies and wavenumbers of pure rotational and vibration-rotational spectra

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By relating non-adiabatic effects, evaluated from analysis of only frequencies and wavenumbers of pure rotational and vibration-rotational transitions of GeS in several isotopic variants, to electric and magnetic properties, we estimated the electric dipolar moment and rotational g factor of GeS; the sense of electric polarity is 'GeS⁻. These results are compared with published magnitudes from the Stark and Zeeman effects. Among nine parameters to reproduce quantitatively 727 transitions of nine isotopic variants in vibrational states up to v = 7, six parameters serve to define a potential-energy function in the range $1.84 < R/10^{-10}$ m < 2.26; $R_e/10^{-10}$ m $= 2.0120490 \pm 0.0000017$. These results serve as precedents for the estimation of electric and magnetic properties of other molecular systems for which data from Stark and Zeeman effects are unavailable.

1. Introduction

Buckingham wrote [1] that by observing the effects of electric and magnetic fields on free molecules one can measure diverse molecular properties. What we demonstrate in the present work is that by appropriate measurements of molecular spectra in the absence of electric and magnetic fields one can nevertheless derive useful information about electric and magnetic properties of free molecules.

These properties are customarily measured on subjecting appropriate samples (gases at small densities) to externally applied electric and magnetic fields and measuring the response; such fields are generally static or modulated at frequencies less than 1 MHz, even if the response is detected by means of electromagnetic radiation at much greater frequencies. We proposed [2] a method to derive information about electric and magnetic properties of diatomic molecules from only spectra of samples measured in the absence of an externally applied electric or magnetic field; for the first molecular species, GaH, that served to illustrate this method, these spectra involved only vibration-rotational transitions [2], whereas in further instances pure rotational transitions were included in data sets. Results have proved encouraging in that not only magnitudes but also signs of pertinent quantities with respect to molecular frames may be deduced; for electric dipolar moments the precision is only moderate, but chemically meaningful information about the polarity is difficult to acquire otherwise. The method relies on the availability, for multiple isotopic variants of a particular molecular species, of precisely measured frequencies and wavenumbers of spectral transitions that characterize a particular electronic state. Precise measurements are required because pertinent effects, called extra-mechanical, are small; the dominant effect governing these spectra is considered to be the function for internuclear potential energy, which serves as the basis of vibrational and rotational motions,

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according to a description within classical mechanics, of nuclei and their associated electrons and which is formally independent of nuclear mass. Information about electric and magnetic properties is derived from a small additional dependence of transitions of isotopic variants on the mass of an individual nucleus beyond a dependence of measured frequencies and wavenumbers on the reduced mass, which reflects the kinetic energy of vibrating and rotating nuclei.

Diatomic molecules of most species have a permanent electric dipolar moment. Although a free diatomic molecule without net electronic spin or orbital angular momentum (with electronic state of symmetry class ${}^{1}\Sigma^{+}$ or O⁺), and not rotating, lacks a permanent magnetic dipolar moment (apart from any due to intrinsic nuclear angular momenta), rotation of an electrically dipolar molecule about the centre of mass generates a small magnetic dipolar moment. The ratio of the latter moment to the rotational angular momentum is proportional to a (dimensionless) rotational factor g as the coefficient of the nuclear magneton that carries the required units. These moments that are characteristic electric and magnetic properties of electrically neutral molecules are customarily measured accurately by means of Stark and Zeeman effects: spectral lines of a gaseous sample at small pressure subjected to an externally applied electric or magnetic field display splitting in response to those stresses.

Of molecular species already treated according to our method for available spectra of sufficient quality and quantity, for GaH the rotational g factor, g_{1} , was estimated precisely [2], whereas the corresponding estimate of the electric dipolar moment, μ^{e} , was meaningless. No experimental measurement of either g_{J} or μ^{e} of GaH is reported, although a calculation [3] of unknown accuracy yielded a small value of μ^e to which our estimate would have been insensitive, ultimately reflecting the finite precision of the original spectral measurements. A subsequent calculation [S. P. A. Sauer, personal communication] of g_J for ⁶⁹Ga¹H yielded values in the range [-3.44, -3.24], depending on the level of the calculation, consistent with our value $g_{\rm J} = -3.223 \pm 0.011$ [2]. For AlH, despite lack of isotopic species of Al other than ²⁷Al, we estimated $g_J = -2.8 \pm 0.5$ for ²⁷Al¹H, consistent with the result -3.3from a theoretical calculation [4]; this information from the rotational g factor was applied to estimate the perpendicular component of the paramagnetic contribution to the total molecular magnetisability. For molecules containing only massive nuclides, in the case of BrCl the value $\mu^e = (+2.38 \pm 0.78) \times 10^{-30}$ C m [5], corresponding to the polarity 'BrCl- and deduced from only spectral frequencies and wavenumbers, agreed within the specified uncertainty with the more precise magnitude $|\mu^{e}|$ = $(1.732 \pm 0.007) \times 10^{-30}$ C m measured by means of the Stark effect for ⁷⁹Br³⁵Cl and ⁸¹Br³⁵Cl in the vibrational state v = 0 [6]; no measurement of g_3 of BrCl is available for comparison with our estimate $g_J = -0.02509 \pm 0.00070$ for ⁷⁹Br³⁵Cl [5]. For BF, estimate of neither g_{J} nor μ^{e} was practicable [7], but the polarity $^{-}BF^{+}$ indicated by previous calculations [8] was confirmed. Hence there exists no direct comparison of results for both g_J and μ^e from measurements of only frequencies and wavenumbers with both such quantities from other experiments. In the present work we treated sufficiently precise spectral data of GeS to enable just such a comparison; here we describe how we determined both the permanent electric dipolar moment and rotational q factor of GeS from merely frequencies and wavenumbers of spectral lines of several isotopic variants (no data of intensity) of pure rotational and vibration-rotational transitions measured without an applied field.

2. Summary of theoretical basis

According to a comprehensive analytic treatment [9] of adiabatic and nonadiabatic effects and its implementation in an algorithm [10] applied in a computer program 'Radiatom' to reduce many spectral data to few parameters as coefficients of pertinent radial functions, we not only estimated both the magnitudes of the electric dipolar moment and the rotational g factor but also defined their signs; hence, we derived the absolute sense of the electric moment of GeS with respect to the internuclear axis. For this purpose we apply an effective Hamiltonian for motion of nuclei separated a distance R in an electronic state ${}^{1}\Sigma^{+}$ or O⁺, of the form [10]

$$\mathscr{H}_{\rm eff}(R) = \tilde{P}[1+\beta(R)]\,\tilde{P}/2\mu + V(R) + V'(R) + \hbar^2[1+\alpha(R)]\,J(J+1)/(2\mu R^2), \tag{1}$$

involving an operator \hat{P} for the linear momentum of the nuclei; other quantities are defined below. To apply these functions we transform to the reduced displacement variable

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

that possesses the valuable property of remaining finite throughout the range of molecular existence: for $0 \le R < \infty$, $-2 \le z < 2$ [11, 12]. With SI units of wavenumber, the potential energy V(R) independent of nuclear mass we represent in the form [11]

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

For a diatomic molecule AB having nuclei of unlike protonic numbers and reduced mass μ , the remaining functions dependent on individual nuclear masses we represent by means of separate expansions for the atomic centre of each type A and B. In the final term of equation (1) that represents the centrifugal motion of nuclei and their associated electrons, there appears a function $\alpha(R)$ for non-adiabatic rotational effects that take into account that electrons follow imperfectly one or other nucleus in its rotation about the centre of mass [9],

$$\alpha(R) \to \alpha(z) = m_{\rm e} \left[\sum_{j=0} t_j^{\rm a} z^j / M_{\rm a} + \sum_{j=0} t_j^{\rm b} z^j / M_{\rm b} \right].$$
(4)

For non-adiabatic vibrational effects that pertain analogously to vibrational inertia of electrons with respect to the nuclei, the first term on the RHS of equation (1) for the nuclear kinetic energy of motion along the internuclear axis contains a function [9]

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

For adiabatic effects according to which the true internuclear potential energy [i.e., V(R) + V'(R)] depends in general not only in the internuclear distance as V(R) independent of mass but also slightly on the relative momenta of the nuclei, and hence on their masses, the correction term is [9]

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

Energies within a particular electronic state, or vibration-rotational terms of molecular eigenstates, we express in the form [10]

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

in which we suppress explicit isotopic dependence of \tilde{E}_{vJ} and various term coefficients Y_{kl} and Z_{kl} ; the dependence of the latter coefficients on radial coefficients c_j , $s_j^{a,b}$, $t_j^{a,b}$ and $u_i^{a,b}$ according to analytic relations is explained elsewhere [10].

3. Application to spectral data of GeS

The frequency data of GeS to which we applied the program 'Radiatom' consist of 111 pure rotational transitions in total in vibrational states up to v = 5: 20 microwave lines of ⁷⁰Ge³²S [13-15], 22 lines of ⁷²Ge³²S [13-15], four lines of ⁷²Ge³²S and one of ⁷⁴Ge³³S reduced from measured components due to nuclear quadrupolar effects [16], 36 lines of ⁷⁴Ge³²S [13–15], 16 lines of ⁷⁶Ge³²S [13–15], and four lines [14, 15] of each of ⁷⁰Ge³⁴S, ⁷²Ge³⁴S and ⁷⁴Ge³⁴S. The wavenumber data comprise in total 616 vibration-rotational transitions [17]: 114 lines of ⁷⁰Ge³²S, 125 lines of ⁷²Ge³²S, 99 lines of ⁷³Ge³²S, 127 lines of ⁷⁴Ge³²S, 91 lines of ⁷⁶Ge³²S, 8 lines of ⁷⁰Ge³⁴S, 11 lines of ⁷²Ge³⁴S and 41 lines of ⁷⁴Ge³⁴S, in vibrational progressions with $\Delta v = 1$ up to v' = 7. The uncertainties associated with measurement of microwave frequencies are assigned according to standard deviations indicated by original authors [13–16]; each infrared line was assigned an uncertainty 0.060 m⁻¹ consistent with the standard deviation of a fit of these data to spectral parameters [17]. In a simultaneous inversion of all spectral data directly to radial coefficients according to the criterion of the least sum of weighted squares of residuals, the weight of each datum was the reciprocal square of the corresponding uncertainty.

According to an unbiased criterion of the maximum value of the F statistic to select the model, we achieved the best fit with only nine adjustable parameters, with values of all other possible parameters set to zero. The results appear in table 1 as the upper nine values in the column labelled unconstrained fit; these parameters, all formally independent of nuclear mass, include the equilibrium internuclear distance R_e , the equilibrium force coefficient k_e , four coefficients c_j with $1 \le j \le 4$ of the function V(z)representing potential energy (equation (3)), two coefficients $t_0^{\text{Ge}, \text{S}}$ in the function $\alpha(z)$ representing non-adiabatic rotational effects (equation (4)), and one coefficient s_0^{Ge} in the function $\beta(z)$ representing non-adiabatic vibrational effects (equation (5)). The normalized standard deviation $\hat{\sigma}$ of this fit was 0.955, entirely equivalent to that attained in an earlier fit of the same 616 infrared lines but only 91 microwave lines to 10 or 11 other parameters [17]. The maximum range of validity of radial functions in table 1 is $1.84 \le R/(10^{-10} \text{ m}) \le 2.24$.

The parameters $t_0^{a,b}$ of two atomic centres A and B in a diatomic molecule ${}^+AB^-$ having the indicated electric polarity are related to electric dipolar moment μ^e and rotational g factor g_J according to the relations [2]

$$\mu^{\rm e} \approx \frac{1}{2} e R_{\rm e} (t_0^{\rm a} - t_0^{\rm b}), \tag{8}$$

$$g_{\rm J} \approx m_{\rm p} (t_0^{\rm a}/M_{\rm a} + t_0^{\rm b}/M_{\rm b}),$$
 (9)

in which e and m_p are the protonic charge and mass, and M_a and M_b are rest masses of neutral atoms into which the diatomic molecule dissociates. Thus, although μ^e

Property	Unconstrained fit	Constrained fit
$\frac{1}{k_{\rm e}/{\rm N~m^{-1}}}$	433.65833±0.00137	433.65835 ± 0.00137
$R_{a}^{e}/(10^{-10} \text{ m})$	2.0120443 ± 0.0000025	2.0120490 ± 0.0000017
C ₁	-2.059634 ± 0.000030	-2.059663 ± 0.000027
c,	1.937553 ± 0.000185	1.937698 ± 0.000177
c_3	-1.0897 ± 0.0032	-1.0894 ± 0.0032
C,	-0.106 ± 0.028	-0.111 ± 0.028
s_0^{de}	1.36 ± 0.41	1.36 ± 0.41
t _o ^{Ge}	-1.402 + 0.130	[-1.2138 + 0.0086]
t_0^s	-1.822 ± 0.081	$\begin{bmatrix} -1.6277 \pm 0.0061 \end{bmatrix}$
$\frac{1}{\mu^{e}/(10^{-30} \text{ Cm})}$	6.76+0.79	$[6.671 \pm 0.20]^{b}$
g_{J}^{c}	-0.07702 ± 0.0044	$[-0.06828 \pm 0.00011]^{d}$
	0.955	0.958
<i>F</i> /10 ¹⁴	2.56	3.27

Table 1. Analysis of spectra of GeS according to two approaches.^a

^a Values within brackets are constrained: see text; specified uncertainties signify single estimated standard errors; uncertainties of values of k_e and R_e take into account the uncertainties of pertinent fundamental constants h and N_A .

^b From [14].

^e Parameters are independent of mass except g_{J} that applies specifically to ⁷²Ge³²S.

^d From [18].

remains independent of nuclear mass, g_{J} evidently pertains to a particular isotopic variant according to atomic masses M_{a} and M_{b} . In this way we estimated values of μ^{e} and g_{J} that appear in the first column of table 1. These values of t_{0}^{Ge} and t_{0}^{s} are consistent with only the polarity $+GeS^{-}$.

Measurements of the Stark effect on pure rotational transitions $J = 1 \leftarrow J = 0$ and $J = 3 \leftarrow J = 2$ of ⁷⁴Ge³²S in vibrational state v = 0 yielded only a (mean) magnitude of the electric dipolar moment [14]. Measurements of the Zeeman effect on a pure rotational transition $J = 4 \leftarrow J = 3$ of only ⁷²Ge³²S in the ground vibrational state yielded the magnitude of g_J and, indirectly, its sign [18]. According to these values specified in the second column of table 1, we calculated, according to equations (8) and (9) and assuming the polarity ⁺GeS⁻, values of $t_0^{Ge,S}$ and fitted all 727 spectral transitions with these coefficients so constrained; values of seven adjusted parameters of this constrained fit appear in table 1. This normalized standard deviation is the same as that of the unconstrained fit, but the enhanced F statistic reflects fewer adjustable parameters. Discrepancies between corresponding values of parameters in the two sets lack significance with respect to the larger estimated standard error.

The distinction between equilibrium properties μ^{e} and g_{J} in equations (8) and (9) and their expectation values that correspond to physical measurements is negligible with respect to estimated standard errors of these quantities in the unconstrained fit. The values thus generated confirm magnitudes independently measured more precisely by means of Stark and Zeeman effects. As values of $t_{0}^{\text{Ge},S}$ derived from the latter experiments are more precise than those in our unconstrained fit, parameters of the constrained fit constitute the most compact and most chemically and physically meaningful coefficients of radial functions that reproduce all relevant spectral data of

transition frequencies and wavenumbers of GeS within the accuracy of their measurements. According to results for SiS and other molecules [19, 20], genuinely adiabatic detectable effects are negligible for such massive nuclides; hence, we excluded coefficients $u_j^{\text{Ge,S}}$ from parameters in the sets tested. This approach already proved practical for reproducing the electric dipolar moment of BrCl [5]. Conversely, a satisfactory agreement between values of μ^e and g_J from the literature and those estimated here with neglect of $u_j^{\text{Ge,S}}$ provides further evidence that adiabatic effects that vary with R or z are small relative to non-adiabatic effects for molecules that contain massive nuclides, at least for Ge and S in the present case. Implicit in this procedure is a separate treatment of electronic and nuclear motions, but that we take explicit account of non-adiabatic (and, if necessary, adiabatic) effects implies that our results transcend nominal limitations of this approximation [9, 10].

4. Discussion

Although a quantum-chemical calculation of electric dipolar moment according to methods of molecular electronic structure typically yields both magnitude and sign of this vectorial quantity, most experimental methods for evaluating this quantity provide only the magnitude, most accurately by means of the Stark effect. The conventional approach to decide the sign of this moment, relative to axes fixed in the molecular frame, involves application of the Zeeman effect, specifically variation of the rotational g factor with isotopic mass [21]; such measurements may yield also a rough magnitude of this electric moment. Because the rotational g factor of GeS was measured for only one isotopic variant, the sign of μ^e was not determined [18].

In his monograph on electric and magnetic susceptibilities [22], van Vleck discussed the relation of electric dipolar moments to the intensities of spectral lines associated with pure rotational transitions; in a treatment [23] of adiabatic and non-adiabatic effects in connection with isotopic corrections in molecular spectra, he alluded only indirectly to the relation between the sum of electronic matrix elements over excited states and magnetic susceptibility. In that work the concept of a rotational q factor was absent. In the present work we relate these electric and magnetic properties of the diatomic molecule GeS to frequencies and wavenumbers of specified spectral lines through a quantitative treatment of non-adiabatic effects. Our evaluation of the electric dipolar moment and rotational q factor by this means yields directly both their magnitudes and their signs; although these values are less accurate than those derived from application of the Stark and Zeeman effects [14, 18], this accuracy reflects ultimately the finite precision and accuracy of available spectral data. That the electric dipole has the sense 'GeS⁻ is thus established for this particular molecule by means of only frequency data of pure rotational transitions and wavenumbers of vibrationrotational transitions measured in the absence of electric and magnetic fields. Although the present application involves a net electrically neutral molecule, the method is evidently applicable also to molecular ions for which experiments with the Stark and Zeeman effects are problematic.

In summary, this demonstration that the electric dipolar moment and rotational g factor deduced from measurements of frequencies and wavenumbers of transitions in pure rotational and vibration-rotational spectra agree reasonably well with those from Stark and Zeeman effects provides a basis for application of this approach to other molecules for which spectral data of sufficient quality and quantity are available but for which these electric and magnetic properties are not separately measured.

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