# NEW TESTS OF MODELS IN CHEMICAL BINDING – EXTRA-MECHANICAL EFFECTS AND MOLECULAR PROPERTIES

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## Abstract

We examine the validity of two models according to which we derive information about structural, dynamic, electric and magnetic properties of small molecules from analysis of frequency data of vibration-rotational spectra in absorption or emission. One model is the atomic approximation, according to which we associate with a particular atomic centre (atomic nucleus) electrons of number approximately equal to the protonic number of the nucleus; by this means we derive structural and dynamic information. Another model of the diatomic molecule is a rotating electric dipole, according to which parameters associated with extra-mechanical (adiabatic and nonadiabatic) effects yield information about electric and magnetic properties, namely the permanent electric dipolar moment and the rotational *g* factor. Spectral data of LiH and GeS are employed as tests of these models, on the basis of which evaluation of these properties proves practicable for other small molecules, for which illustrations are presented.

## INTRODUCTION

Molecular spectra that consist of discrete lines measured at great resolution provide much information, initially in the forms of frequencies of line centres, integrated intensities of individual lines and shapes of lines, that with the aid of theories and models yield data about properties both of discrete molecules and of their collection in the macroscopic sample. If spectra are measured under conditions of temperature and total density such that intermolecular interactions are considered negligible, the line shape holds little interest. Frequencies may then be measured with great precision: the ratio of the uncertainty of measurement to the line frequency approaches commonly parts in $10^7$ and in the best cases even parts in $10^{10}$; according to Bohr's relation these frequencies that characterise the energies of the photons are proportional to differences of energies of various eigenstates of the molecule. Intensities are still subject to relatively poor precision: the ratio of the uncertainty of measurement to the integrated intensity typically approaches only parts in $10^2$; these intensities are proportional to probabilities of transitions between eigenstates. If spectra of interest involve transitions within one particular electronic state, then all properties deduced from these spectra pertain

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primarily to that electronic state; accordingly this state becomes characterised. According to an explanation in terms of classical mechanics, such optical spectra of free molecules are associated with vibrational and rotational motions of nuclear centres and their associated electrons. In treating spectra in terms of such motions according to mechanics either classical or quantal, one introduces conventionally the idea of molecular structure as a fairly rigid arrangement of atomic centres in space of three dimensions: the position of a nucleus defines the location of that atomic centre, and the mass of a nucleus and of electrons of number about the protonic number of that nucleus so as to bestow almost electric neutrality define masses of the atomic centres. This model enables us to deduce parameters that describe structural and dynamic properties, or the mechanical effects, of the molecules within the classical model of its structure. To the extent that electrons fail to follow exactly one or other nucleus in their motions, this model is quantitatively inadequate. Spectral repercussions of this condition we attribute to extra-mechanical effects, classified as adiabatic or nonadiabatic for reasons to be explained. With the aid of a second model, that of a rotating electric dipole, we can analyse nonadiabatic rotational effects to derive parameters that pertain to electric and magnetic properties of the free molecule and to their collection within the macroscopic sample. In what follows we explain the application of these two models to a diatomic molecule; this term implies a collection of particles comprising two atomic nuclei and their associated electrons but not necessarily net electric neutrality of the molecular species. The reason that this applicability is limited to diatomic molecules is that sophistication of treatment of spectra is naturally in inverse proportion to the number of nuclei within a molecular carrier of those spectra. In analyses of vibration-rotational spectra of molecules containing three or more nuclei, formal separation of vibrational and rotational motions becomes increasingly difficult: vibrational angular momentum, vibrational and intricate vibration-rotational interactions greatly complicate these analyses. At present some progress is made for linear triatomic molecules, but at the expense of an analytic treatment that yields maximal physical insight.

After a summary of an applicable mathematical formalism, we test first the applicability of the notion that molecular structure is based on atomic centres, and then proceed to derive electric and magnetic properties based on the understanding of extra-mechanical effects.

## THEORETICAL BASIS

For an assembly of two atomic nuclei A and B, designated by subscripts 'a' and 'b' and having masses $M_a$ and $M_b$ and charges $+Z_a$ and $+Z_b$ in units of the protonic charge respectively, and $N$ electrons, each of mass $m_e$ and charge $-1$ in the same units, the hamiltonian of minimal length contains terms for kinetic energies of electrons and of nuclei and for potential energies of coulombic attraction between nuclei and electrons and of repulsion between electrons and between the nuclei[1].

$$\mathcal{H} = \frac{-\hbar^2}{2m_e}\sum_{j=1}^{N}\nabla_j^2 - \frac{1}{2}\hbar^2\sum_{l=a,b}\nabla_l^2/M_l - \frac{e^2}{4\pi\varepsilon_0}\left[\sum_{j=1}^{N}\sum_{l=a,b}\frac{Z_l}{r_{jl}} - \sum_{j=1}^{N}\sum_{k>j}^{N}\frac{1}{r_{jk}} - \frac{Z_aZ_b}{R}\right] \tag{1}$$

Because the only parameters in this hamiltonian are masses and charges of constituent particles of a molecule, eigenvalues of this expression enable no characterisation of a particular electronic state according to analysis of pertinent molecular spectra. For this reason we invoke a conventional classical notion of molecular structure according to which we distinguish a distance between two particular constituent particles, namely $R$ as the instantaneous internuclear distance. We suppose that discrete spectra of interest imply a stable electronic state with a characteristic equilibrium internuclear distance $R_e$ at which the internuclear potential energy is a minimum. Under these conditions we postulate the following effective hamiltonian to describe molecular motions relative to the origin of a coordinate system at the centre of molecular mass.

$$\mathcal{H}_{\mathrm{eff}}(R) = \hat{P}[1+\beta(R)]\hat{P}/(2\mu) + V(R) + [1+\alpha(R)][J(J+1)]h^2/(8\pi^2\mu R^2) \qquad (2)$$

The first term represents kinetic energy of atomic centres, the second denotes interatomic potential energy and the third takes into account centrifugal motion of atomic centres about the origin at the centre of molecular mass. The first and third terms contain explicitly the reduced atomic mass $\mu = M_a M_b/(M_a + M_b)$. The interatomic potential energy comprises three terms,

$$V(R) = V^{\mathrm{BO}}(R) + V^{ad}(R) + V^{na}(R) \qquad (3)$$

of which the first is independent of mass.

We explain the various terms as follows. If the diatomic molecule were to consist of only two structureless 'atoms', being two point masses separated a distance $R$, the terms $\beta(R)$, $\alpha(R)$, $V^{ad}(R)$, $V^{na}(R)$ and any further contributions to the preceding two expressions would be absent; hence these terms take into account the fact that electrons fail to follow perfectly one or other nucleus during rotational and vibrational motions of nuclei. As vibrational potential energy depends in general not only on the distance between nuclei, in $V^{\mathrm{BO}}(R)$, but also slightly on relative momenta of nuclei – hence on their individual masses, the term $V^{ad}(R)$ embodies this correction. All three terms $\beta(R)$, $\alpha(R)$ and $V^{ad}(R)$ contain implicitly a ratio of electronic (rest) mass $m_e$ to a nuclear (or a reduced nuclear) mass to the power unity relative to adjacent terms[1], made explicit in subsequent equations, whereas the further terms $V^{na}(R)$ and others that might appear in an extended treatment[2] contain such a ratio to a power greater than unity. As this ratio of masses is much smaller than unity and as corresponding contributions to molecular energies from such further terms are negligible by comparison with present accuracy of almost all measurements of transition frequencies, we eliminate such terms from present consideration; in practice, retained terms thereby absorb effects of these neglected terms that might prove significant in current experiments. In a derivation of this effective hamiltonian[2], the radial function $V^{ad}(R)$ is shown to represent expectation values of various operators within an electronic state of interest, namely the electronic state within which the vibrational and rotational transitions occur, which is typically the ground electronic state; for electrically neutral molecular species to be discussed here for which the hamiltonians in equations 1 and 2 suffice this electronic state belongs to symmetry class $^1\Sigma^+$ or $O^+$. In contrast radial functions $\alpha(R)$ and $\beta(R)$, which represent inertia of electrons with respect to rotational and vibrational motions of nuclei respectively, represent matrix elements[2] of operators (analogous to those in the expectation values of $V^{ad}(R)$) between an electronic state of interest and excited electronic states, correspondingly belonging to symmetry classes $^1\Pi$ or 1 for $\alpha(R)$ and $^1\Sigma^+$ or $O^+$ for $\beta(R)$. For this reason effects within the same electronic state that $V^{ad}(R)$ represent are called adiabatic, whereas interactions between electronic states that $\alpha(R)$ and $\beta(R)$ represent formally generate nonadiabatic rotational and nonadiabatic vibrational effects, respectively. Although these adiabatic and nonadiabatic effects are mathematical artefacts due to special treatment of nuclear motion, not really physical in origin, some effects are related to significant phenomena, to be discussed.

For convenience, we introduce instead of $R$ a reduced variable $z$ [3,4] for displacement from equilibrium separation $R_e$, such that

$$z = 2(R - R_e)/(R + R_e) \qquad (4)$$

which possesses the valuable property of remaining finite throughout the range of molecular existence: for $0 < R < \infty$, $-2 < z < 2$. Henceforth with units of wavenumber for potential and other energies in conformity with spectral convention, the potential energy independent of nuclear mass becomes

$$V^{\mathrm{BO}}(R) \to V^{\mathrm{BO}}(z) = c_0 z^2 (1 + \sum_{j=1} c_j z^j) \tag{5}$$

and a correction for adiabatic effects is expressed

$$V^{ad}(R) \to V^{ad}(z) = (m_e/M_a) \sum_{j=1} u_j^a z^j + (m_e/M_b) \sum_{j=1} u_j^b z^j \tag{6}$$

Remaining pertinent radial functions are, for nonadiabatic rotational effects,

$$\alpha(R) \to \alpha(z) = (m_e/M_a) \sum_{j=0} t_j^a z^j + (m_e/M_b) \sum_{j=0} t_j^b z^j \tag{7}$$

and for nonadiabatic vibrational effects,

$$\beta(R) \to \beta(z) = (m_e/M_a) \sum_{j=0} s_j^a z^j + (m_e/M_b) \sum_{j=0} s_j^b z^j \tag{8}$$

Coefficients $c_j$ for potential energy and $u_j^a$ and $u_j^b$ for adiabatic effects are in principle independent parameters, but coefficients $t_j^a$ and $t_j^b$ are more directly inter-related through other quantities, to be discussed; $s_j^a$ and $s_j^b$ are likewise inter-related.

With these terms in the hamiltonian, we express energies within a particular electronic state, or vibration-rotational terms of molecular eigenstates, according to an expression[5]

$$E_{vJ} = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl}^{v,a} + Z_{kl}^{v,b} + Z_{kl}^{r,a} + Z_{kl}^{r,b})(v + \tfrac{1}{2})^k [J(J+1)]^l \tag{9}$$

in which explicit dependence of $E_{vJ}$, $Y_{kl}$ and various $Z_{kl}$ on nuclear masses in a particular isotopic species is suppressed. How these term coefficients $Y_{kl}$ and $Z_{kl}$ depend on radial coefficients $c_j$, $s_j^{a,b}$, $t_j^{a,b}$ and $u_j^{a,b}$ according to analytic relations is explained elsewhere[5]: in essential summary, coefficients $Y_{kl}$ depend on reduced atomic mass $\mu$, on $R_e$ and on potential-energy coefficients $c_j$; coefficients $Z_{kl}^v$ take into account additional vibration-rotational effects that depend on the individual mass of atomic centre A or B, $M_a$ or $M_b$ respectively, and depend too not only on $c_j$ but also on $s_j$ and $u_j$ of A or B, whereas coefficients $Z_{kl}^r$ that take into account further rotational effects of an individual atomic centre A or B depend on the mass of A or B, on $c_j$, and on $s_j$ and $t_j$ of A or B. According to this scheme, coefficients $c_j$ with $j > 0$, $s_j$ and $t_j$ have typically magnitudes of order unity and are dimensionless, whereas $c_0$ and $u_j$ have magnitudes of order $B_e/\gamma^2$ and dimensions conventionally of wavenumber; here $\gamma$ is a dimensionless ratio of the limiting interval $2B_e$ between successive lines in a pure rotational band to the limiting interval $\omega_e$ between vibrational bands in a sequence, and takes values in a range [0.0001, 0.026] for known molecules in their electronic ground states, with $B_e$ the equilibrium rotational parameter. Relations for $Y_{kl}$ in terms of $c_j$ that are coefficients of $z^j$ are equivalent to those reported by Dunham[6] in terms of $a_j$ that are coefficients of $x^j$; $x = (R - R_e)/R_e$, which lacks a finite value as $R \to \infty$. The fact that vibration-rotational terms $E_{vJ}$ containing only term coefficients $Y_{kl}$ failed to represent accurately effects of mass scaling in molecular spectra of isotopic variants led van Vleck to delineate[7] adiabatic and nonadiabatic effects that are represented here in additional term coefficients $Z_{kl}$.

An alternative formula for vibration-rotational terms

$$E_{vJ} = \sum_{k=0} \sum_{l=0} U_{kl} \mu^{-(k/2+l)} [1 + m_e(\Delta_{kl}^a/M_a + \Delta_{kl}^b/M_b)](v + \tfrac{1}{2})^k [J(J+1)]^l \tag{10}$$

has an empirical basis[8], which is underpinned theoretically[1]. To understand the relationship between parameters in equations 9 and 10, we explain that term coefficients in each set $Y_{kl}$ or various $Z_{kl}$ are expressed as a sum of contributions; rapidly decreasing magnitudes of successive contributions generally ensure acceptable convergence. Thus

$$Y_{kl} = Y_{kl}^{(0)} + Y_{kl}^{(2)} + Y_{kl}^{(4)} + \ldots \tag{11}$$

in which each successive contribution contains a further factor $\gamma^2$. The leading term $Y_{kl}^{(0)}$ contains the reduced atomic mass $\mu$ to a power $-(k/2+l)$; defined as $Y_{kl}^{(0)}\,\mu^{(k/2+l)}$, $U_{kl}$ then becomes formally independent of mass. Parameters $\Delta_{kl}$ of atomic centre A or B, which are also formally independent of mass, are likewise evidently related to $Y_{kl}^{(2)}$ and to the sum of all $Z_{kl}$ (or to at least their leading terms $Z_{kl}^{(0)}$ ). Further terms containing $(m_e/M_j)^2$, $j = a$ or $b$, etc. that might be included in equation 10 are not yet needed in relation to uncertainties of measurements of transition frequencies. As we accordingly truncate equation 10, we correspondingly truncate equation 11 after $Y_{kl}^{(2)}$ and the analogous relations for $Z_{kl}$ after $Z_{kl}^{(0)}$, because the ratio of electronic and nuclear masses, $m_e/M_j$, $j = a$ or $b$, has a magnitude of the order of $\gamma^2$.

A physical but qualitative explanation of the nature of adiabatic and nonadiabatic effects follows. Although one formally considers vibrational and rotational motions of molecules to involve primarily nuclei – indeed some theoretical treatments are based rigorously on that premise, in practice only relatively imprecise values of nuclear masses are available for most nuclides; to match the precision of typical relevant spectral data one has perforce to use atomic masses. If electrons followed perfectly one or other nuclei (so as to maintain effective near neutrality of charge about each atomic centre), terms $V^{ad}(R)$, $\alpha(R)$ and $\beta(R)$ in equations 2 and 3 would be superfluous. One might imagine that electrons outside a region between nuclei can follow well the motion of the nearer nucleus because of strong electrostatic attraction; as electrons between nuclei would likewise be attracted to both nuclei, they might tend to follow neither nucleus. The effective mass of each atomic centre would then differ from that of the isolated neutral atom; terms $\alpha(R)$ and $\beta(R)$ thereby constitute corrections to these atomic masses to take account of this nominally physical effect, and the radial dependence reflects that effective atomic mass depends on internuclear distance. As 'valence' electrons are indistinguishable from electrons of any other purported kind, this explanation is qualitative but may assist one to appreciate the magnitude of adiabatic and nonadiabatic effects despite their artefactual nature.

According to the preceding argument, from spectra of a molecule containing atomic centres characterised with distinct atomic numbers one can derive information of two types – dependence of vibration-rotational terms on mass of each atomic centre separately (rather than on merely the reduced atomic mass), and further rotational effects. Terms within the hamiltonian that yield these components of eigenenergies number three – adiabatic, nonadiabatic rotational and nonadiabatic vibrational. For this reason one cannot in general evaluate separately these effects from only frequencies of transitions of diatomic molecules of multiple isotopic variants applicable to samples of which spectra are measured in the absence of an externally applied electric or magnetic field. There exists however a magnetic interaction of rotating molecules that lack net electronic spin or orbital angular momentum in their rotationless states (electronic state of symmetry class $^1\Sigma^+$ or $O^+$). Under conditions of appropriate alignment of the magnetic field, this Zeeman effect produces a splitting of lines, the extent of which is proportional to a molecular parameter called the rotational $g$ factor, which is formally an expectation value of a particular vibration-rotational state[9]. In principle, on analysis of such data for many and varied vibration-rotational states one can generate precisely the radial function $\alpha(R)$, but in practice measurements of $g_J$ are common for only the rotational state $J = 1$, and seldom for other than the vibrational ground state $v = 0$.

## EVALUATION OF ADIABATIC AND NONADIABATIC EFFECTS FOR LiH

The diatomic species LiH, which exists as a stable molecular compound in the gaseous phase in equilibrium with the ionic crystalline substance at temperatures above about 800 K, presents in principle an excellent opportunity to examine adiabatic and nonadiabatic effects according to the preceding discussion: because isotopic variants of both Li ($^6$Li and $^7$Li) and H (actually $^1$H and $^2$H, and prospectively even $^3$H) are available and because these nuclei are relatively light, these effects might be expected to be more readily detected for this compound than for others. The rotational $g$ factor is measured accurately for both $^7$Li$^1$H and $^7$Li$^2$H [10], but for only one rotational state in the vibrational ground state (i.e. $v = 0, J = 1$); a qualitative indication of the rotational variation of $g_J$ is available from other measurements[11]. Available spectra include pure rotational transitions in the millimetre-wave and far infrared regions and vibration-rotational transitions in the mid infrared region corresponding to the progression $\Delta v = 1$, for four isotopic variants containing stable nuclei, as described in detail elsewhere[12]. Although these spectral data have smaller precisions than those for the best measurements on comparable compounds, they serve to illustrate the approximate orders of magnitudes of pertinent effects, provided that we combine them with calculated information about the radial dependence of the rotational $g$ factor, as available experimental data[10,11] are too sparse.

To employ meaningfully these data to discern the sought magnitudes we consider the ratio of contributions to $Z^v_{kl}$ and $Z^r_{kl}$ of each nuclear type to $Y_{kl}$, and further we divide this ratio by the quotient of electronic and atomic masses. The reason for this approach is that according to a theoretical analysis, developed first by Born and Oppenheimer and later clarified and extended[13], we expect these adiabatic and nonadiabatic effects to exhibit such relative magnitudes involving the ratio of $m_e$ and a nuclear (or atomic) mass $M_a$ or $M_b$, as is clear from the comparison of equations 9 and 10. Accordingly, in table 1 we present the quantities $(Z_{kl}/Y_{kl})/(m_e/M_j)$, for various contributions to $Z_{kl}$, for various values of $k$ and $l$ for which data are available[14], and for two atomic centres, $j$ = Li and H, in $^7$Li$^1$H.

The most important conclusion from these results is that ratios of components of extra-mechanical effects to mechanical effects have indeed magnitudes of the order of the ratio of the electronic to an atomic (or nuclear) mass, although there appears to be a significant trend of increased magnitude in the sequence with $k = 0$ and increasing $l$ of LiH. Apart from exact cancellation of nonadiabatic vibrational effects in $Z^r_{kl}$ with those in $Z^v_{kl}$ for $k = 0$ previously noted[5], one discerns that adiabatic, nonadiabatic rotational and nonadiabatic vibrational contributions to extra-mechanical effects in LiH have comparable orders of magnitude, whereas those adiabatic effects that vary with internuclear distance in SiS have magnitudes too small to be discerned from available spectral data; adiabatic effects that do not vary with internuclear distance are undetectable from these spectral analyses. In the case of CO, adiabatic contributions are detectable but their magnitudes seem consistently smaller than those of nonadiabatic rotational and nonadiabatic vibrational contributions[15]. Thus for vibration-rotational states in the electronic ground state far from the limit of the least energy of dissociation to neutral atomic fragments in their appropriate electronic states, the approximation of atomic centres within a molecule is proved to have an extent of validity expected according to work of Born, Oppenheimer, Fernandez and others[13]. A classical model of a molecule as a fairly rigid arrangement of 'atoms' in space is hereby justified for vibration-rotational states of diatomic molecules well below the dissociation limit within the expected range of validity, although there remains no implication from these results that within molecules there exist atoms

**Table 1.** Ratio of adiabatic (ad), nonadiabatic rotational (nr) and nonadiabatic vibrational (nv) contributions to extra-mechanical term coefficients $Z_{kl}$ to the corresponding mechanical term coefficient $Y_{kl}$, divided by the ratio of electronic to atomic mass.[a]

| | | $Z^r_{kl}$ | | $Z^v_{kl}$ | |
|---|---|---|---|---|---|
| Li in $^7$Li$^1$H | | | | | |
| $k$ | $l$ | nr | nv | ad | nv |
| 0 | 1 | 0.77 | ... | −0.87 | ... |
| 0 | 2 | −0.95 | 0.67 | −1.75 | −0.67 |
| 1 | 0 | ... | ... | −0.42 | 0.33 |
| H in $^7$Li$^1$H | | | | | |
| 0 | 1 | −0.75 | ... | −0.81 | ... |
| 0 | 2 | −2.72 | −0.30 | −1.36 | 0.30 |
| 0 | 3 | −7.30 | −1.09 | −2.41 | 1.09 |
| 0 | 4 | −13.2 | −2.04 | −3.27 | 2.04 |
| 1 | 0 | ... | ... | −0.52 | −0.15 |
| 1 | 1 | −0.04 | 0.11 | −0.49 | −0.14 |
| 1 | 2 | 2.26 | 0.39 | ... | −1.13 |
| 2 | 0 | ... | ... | ... | −0.49 |
| 2 | 1 | ... | 0.18 | ... | ... |
| Si in $^{28}$Si$^{32}$S | | | | | |
| 0 | 1 | −1.17 | ... | ... | ... |
| 1 | 0 | ... | ... | ... | 0.88 |
| S in $^{28}$Si$^{32}$S | | | | | |
| 0 | 1 | −1.55 | ... | ... | ... |
| 1 | 0 | ... | ... | ... | −0.16 |

[a] The mark ... indicates that the pertinent quantities are indeterminate.

(that have a 'shape', 'volume' or other property of an isolated, electrically neutral atom in the gaseous phase).

## APPLICATION OF THE MODEL OF A ROTATING DIPOLE

According to this model two stationary point masses, $M_a$ and $M_b$, carry charges of equal magnitude but opposite sign, $+q$ and $-q$ respectively, and are separated a distance $R_e$. This stationary dipole possesses electric dipolar moment $\mu^e$ and exerts an electric field but no magnetic field relative to axes fixed in space. If such a dipole rotates about its centre of mass, the rotation of each separate pole is equivalent to an electric current in a loop of a conductor; each such loop generates a magnetic field. To the extent that masses $M_a$ and $M_b$ are not equal, the radii of the two loops differ and the magnetic fields thus fail to cancel one another. This net magnetic field implies the existence of a magnetic dipole, of which the magnetic dipolar moment is proportional to the rotational angular momentum of the rotating masses; the factor of proportionality involves the nuclear magneton, to carry units, and a rotational $g$ factor that thereby lacks dimensions. For a rotating diatomic molecule as a rotating electric dipole, molecular rotation is supposed to induce an interaction with electronically excited states; if the electronic ground state lacks net electronic spin or orbital angular momentum, belonging to symmetry class $^1\Sigma^+$ or $O^+$, the rotational motion induces interaction with excited states of symmetry class $^1\Pi$ or 1; we ignore the effects of net intrinsic nuclear angular momentum. According to the relation[16]

$$g_J = g_J^{nr} + m_p|\mu^e|(1/M_a - 1/M_b)/(eR_e) \tag{12}$$

the rotational $g$ factor contains two contributions, the former from inertia of electrons with respect to rotating nuclei or nonadiabatic rotational effects, and the latter due to a rotating electric dipole of moment having magnitude $|\mu^e|$ with a positive pole of mass $M_a$ separated from the negative pole of mass $M_b$ by a distance $R_e$; $e$ is the charge on the proton and $m_p$ its mass. When a rotating diatomic molecule interacts with an externally applied magnetic field appropriately oriented, spectral lines associated with pure rotational transitions become split; the extent of splitting depends on the rotational $g$ factor, but direct determination of the sign may require a circularly polarised magnetic field. Although the vibrational dependence of $g_J$, formally an expectation value of a particular vibration-rotational state, is detectable in conventional experiments involving the Zeeman effect, rotational dependence presses present limits of sensitivity.

The relation between the radially dependent rotational $g$ factor, of which the expectation value is measurable, and radial functions defined above is expressed as

$$g_J(R)(m_e/m_p) = m_e \left[ \sum_{j=0} t_j^a z^j/M_a + \sum_{j=0} t_j^b z^j/M_b \right] \tag{13}$$

Making use of an approximation that rotational and vibrational dependences of the rotational $g$ factor are commonly small for not too highly excited rotational and vibrational states, we partition expectation value $g_J$ between atomic centres A and B according to the convention of polarity ($A^+$ and $B^-$):

$$t_0^a = \mu[g_J/m_p + 2|\mu^e|/(eR_eM_b)] \tag{14}$$

$$t_0^b = \mu[g_J/m_p - 2|\mu^e|/(eR_eM_a)] \tag{15}$$

Applicable directly to only electrically neutral diatomic molecules, these relations provide a practical means to interpret radial coefficients $t_0^a$ and $t_0^b$ evaluated by fitting frequencies of pure rotational and vibration-rotational transitions in terms of fundamental molecular properties $g_J$ (dependent on reduced mass of a particular isotopic variant) and $\mu^e$ (independent of molecular mass for a net electrically neutral molecule). (To obtain nonadiabatic rotational contributions to vibration-rotational terms of LiH employed to generate table 1, we used calculated values[17] of $g_J$ and $\mu^e$ as a function of R and fitted radial coefficients $t_0^a$ and $t_0^b$ to combinations of these functions according to these equations 14 and 15 in more general form.)

We applied this approach to estimate the electric dipolar moment and rotational $g$ factor of GeS by fitting available spectral data by means of radial coefficients or equivalent parameters. Because only frequency data even for multiple isotopic variants are inadequate to estimate all adiabatic and nonadiabatic rotational and vibrational effects, we neglect adiabatic effects according to the justification already presented, as both Ge and S have relatively massive nuclides. Then by fitting 727 assorted spectral data (Ogilvie, to be published) we evaluated ten parameters specified in the following table.

All these parameters are independent of nuclear mass; the first seven define the function for potential energy within the range of internuclear distance $1.84 < R/10^{-10}$ m $< 2.26$, as the force coefficient $k_e$ (related[5] to $U_{1,0}$ or $c_0$) indicates the curvature of this function at the distance $R_e$ (related[5] to $U_{0,1}$) of minimum potential energy; the five coefficients $c_j$ define the shape of the function. Three other parameters pertain, in $s_0^{\mathrm{Ge}}$, to nonadiabatic vibrational effects of Ge and, in $t_0$ of Ge and S, to nonadiabatic rotational effects of each separate atomic centre. When we insert the fitted values of $t_0^{\mathrm{Ge}}$ and $t_0^{\mathrm{S}}$ into relations 14 and 15 above, solution of two simultaneous equations yields values $\mu^e/10^{-30}$ Cm $= 7.13 \pm 0.86$ (independent of isotopic variant) and $g_J = -0.07699 \pm 0.0064$ for specifically $^{72}\mathrm{Ge}^{32}\mathrm{S}$. As both $t_0^{\mathrm{Ge}}$ and $t_0^{\mathrm{S}}$ are signed quantities, they are consistent with only a relative polarity $^+\mathrm{GeS}^-$, with the permanent electric dipolar moment having the indicated magnitude. Likewise according to this

**Table 2.** Parameters of GeS derived from spectral data

| property | fitted value |
|---|---|
| $k_e/N\,m^{-1}$ | $433.65847 \pm 0.00136$ |
| $R_e/10^{-10}\,m$ | $2.0120442 \pm 0.0000025$ |
| $c_1$ | $-2.059743 \pm 0.000062$ |
| $c_2$ | $1.93805 \pm 0.00031$ |
| $c_3$ | $-1.0611 \pm 0.0152$ |
| $c_4$ | $-0.329 \pm 0.119$ |
| $c_5$ | $3.89 \pm 0.73$ |
| $s_0^{Ge}$ | $1.39 \pm 0.41$ |
| $t_0^{Ge}$ | $-1.385 \pm 0.130$ |
| $t_0^{S}$ | $-1.828 \pm 0.081$ |

novel interpretation of available spectral data that consist of only frequencies of pure rotational and vibration-rotational transitions, the rotational $g$ factor has both a negative sign and the indicated magnitude.

For $^{74}Ge\,^{32}S$ measurements of the Stark effect in vibrational state $v = 0$ on pure rotational transitions $J = 1 \leftarrow 0$ and $J = 3 \leftarrow 2$ yielded a mean expectation value of electric dipolar moment; the magnitude is $(6.671 \pm 0.20) \times 10^{-30}$ C m[18]. Separate measurement of the Zeeman effect on pure rotational transition $J = 4 \leftarrow 3$ of $^{72}Ge\,^{32}S$ yielded an expectation value of the rotational $g$ factor in the vibrational ground state, specifically the magnitude of $g_J$ and, indirectly, its sign; the value is $-0.06828 \pm 0.00011$[19]. Magnitudes of $\mu^e$ and $g_J$, and the sign of $g_J$, deduced according to only frequency data of spectra measured for samples without externally applied electric or magnetic field as discussed above, agree with these values from application of Stark and Zeeman effects, although the latter are much more precise. Uncertainties of these values deduced from $t_0^{Ge}$ and $t_0^{S}$ have orders of magnitude expected from the known precision of spectral measurements and the relative magnitudes of mechanical and extra-mechanical effects, as explained above for LiH. As the electric dipolar moment is derived from the difference of two quantities $t_0^{Ge}$ and $t_0^{S}$ that both have negative signs, its uncertainty is particularly sensitive to the uncertainties of these quantities, whereas, being derived from a weighted sum of $t_0^{Ge}$ and $t_0^{S}$, $g_J$ is more immune from accumulated uncertainties. If precise experimental values (or at least magnitudes) of $\mu^e$ and $g_J$ are available (such as from application of Stark and Zeeman effects), a preferable procedure in spectral analysis is naturally to constrain $t_0^{Ge}$ and $t_0^{S}$ to their values consistent with the further data; other spectral parameters thereby assume greater 'physical' significance: such a preferred set of spectral parameters is to be presented elsewhere. In cases of either freely fitted or constrained values of $t_0^{Ge}$ and $t_0^{S}$, all spectral data of GeS are equally well reproduced within the accuracy of their measurement: the normalised standard deviation of both fits is 0.95.

As this procedure becomes empirically justified through this successful application to GeS, we applied it to predict unmeasured values of $\mu^e$ and $g_J$ of other molecules. In the case of GaH for which only vibration-rotational spectral data were available, the difference of values of $t_0^{Ga}$ and $t_0^{H}$ were so small, relative to their combined estimated standard errors, that the magnitude of electric dipolar moment derived from their difference lacked significance. However the value of $g_J$ was well defined, $-3.223 \pm 0.011$ for $^{69}Ga^1H$; this value agrees satisfactorily with values in the range $[-3.44, -3.24]$ depending on the level of the quantum-chemical calculation (S.P.A. Sauer, to be published). The first such prediction of $g_J$ was made for AlH on the basis of relatively imprecise spectral measurements on $^{27}Al^1H$ and $^{27}Al^2H$; that value $-2.2 \pm 0.25$[20] for $^{27}Al^1H$ became revised to $-2.7 \pm 0.5$[21] when more precise spectral data were included in the analysis. In both cases lack of isotopic variant of Al made results relatively insensitive to the data, thus somewhat unreliable. Nevertheless it proved practicable to apply the latter value to estimate the paramagnetic contribution to the perpendicular component of the molecular magnetisability. The total magnetisability includes the diamagnetic contribution that was calculated for lack of experimental data; in this case the total perpendicular component of magnetisability $0.4 \times 10^{-28}$ J $T^2$ has a small positive value, thus indicating a (marginally) net paramagnetic value as predicted theoretically, although the overall magnetic susceptibility is negative, consistent with a net diamagnetic property. This net paramagnetic component for AlH is the first experimental evidence, albeit indirect, for the overall paramagnetic susceptibility of BH predicted on the basis of quantum-chemical computations[22]. All three hydrides BH, AlH and GaH of elements of group 13 have electronic ground states of symmetry class formally $^1\Sigma^+$ or $O^+$, which are customarily associated with neither net unpaired electrons nor net orbital angular momentum, thus with diamagnetic susceptibility, apart from effects of net nuclear angular momenta. Preliminary analysis of spectral data of a hydride of a further element in this group indicates that $g_J$ of InH is much less negative than $-3$, although the quality and consistency of data and the relatively decreased influence of mass effects between $^{113}$In and $^{115}$In preclude at present a definitive evaluation. For another member of diatomic hydrides in the family of elements in group 13, TlH, spectral data of insufficient quality and quantity preclude at present a corresponding analysis.

Spectral data of BrCl in its four isotopic variants enabled the deduction of both electric and magnetic properties, according to the procedure applied to data of GeS. Here the relatively small and imprecise difference between $t_0^{\mathrm{Br}}$ and $t_0^{\mathrm{Cl}}$ yielded a correspondingly imprecise value of electric dipolar moment, $\mu^e/10^{-30}$ C m $= 2.38 \pm 0.78$[23], but that value is consistent with the magnitude $1.732 \pm 0.007$[24] from measurement of the Stark effect. For comparison with the more significant value $g_J = -0.02509 \pm 0.00070$ no measurement of the Zeeman effect is reported. The relative electric polarity $^+$BrCl$^-$ from these spectral data conforms to traditional chemical ideas.

In a systematic analysis[25] of available pure rotational and vibration-rotational spectra of fluorides of all elements of group 13 – BF, AlF, GaF, InF and TlF – data from Stark and Zeeman effects serve to constrain values of $t_0^a$ and $t_0^b$ of the latter four molecular species, whereas in the lack of such experimental data for BF values of $g_J$ and $\mu^e$ derived from quantum-chemical computations were applied. According to such calculations[26], the sense of electric dipolar moment of AlF is $^+$AlF$^-$; analogous polarity is expected for succeeding members of this family. Although adiabatic effects are significant for BF, and although lack of isotopic variants of F other than $^{19}$F precludes application of a procedure used successfully for GeS and BrCl, test fits of spectral data of BF indicated the polarity $^-$BF$^+$, perhaps contrary to chemical intuition. This analysis of spectral data uncovered the first experimental evidence in favour of this polarity, long predicted according to quantum-chemical computations[27].

Although spectral data of gaseous carbon dioxide in its several isotopic variants were analysed according to a more numerical approach (maintaining a firm theoretical basis), a value of the rotational $g$ factor was derived[28] from only vibration-rotational spectral data of samples without externally applied electric or magnetic field that agreed with the value from experiments on molecular beams[29]. In the absence of a permanent electric dipolar moment, $g_J$ of $^{12}C\,^{16}O_2$ reflects purely nonadiabatic rotational effects. The assumption in the analysis[28] that adiabatic effects were negligible is justified by the agreement between the two values of $g_J$ from distinct experimental data.

## DISCUSSION

In this work we examine two models, one of great general importance and the other of narrow application. The results in table 1 confirm what chemists and physicists have long taken for granted, namely that the classical idea of a molecule to consist essentially of recognisable atomic centres is a practical model stable compounds under mild conditions. This assumption is least valid for elements of small atomic number; for instance the lengths of bonds between other elements, even those with molar masses as small as that of carbon, are found to be anomalously small according to xray data from diffraction of single crystals because the electronic density near the hydrogen nucleus is comparable with that in the binding region toward an adjacent atomic centre. From a more technical point of view, these results justify the approximation that Born sought to evaluate, first unsuccessfully with Heisenberg, then with increasing refinements published with Oppenheimer and Huang, followed in turn by other workers[13]. Even before the successful treatment, spectroscopists and practitioners of quantum-chemical calculations imposed this separate treatment of nuclear motions on their methods of considering molecular systems drawing their attention. What will prove of increased interest are relative magnitudes of mechanical and extra-mechanical effects for states of a diatomic molecule approaching the dissociation limit. van Vleck[7] expected adiabatic and nonadiabatic vibrational effects to increase with increasing vibrational quantum number. There is in table 1 scant evidence to support this supposition, but the available spectral data of LiH of usable quality pertain to energies only a small proportion of the energy at the first dissociation limit. Precise data of spectral frequencies of vibrational states of much increased quantum numbers and precise expectation values of $g_J$ or accurate computations of $g_J$ and $\mu^e$ over extended ranges of internuclear separation are required to enable tests of relative magnitudes of mechanical and extra-mechanical effects at much greater energies, but LiH remains an excellent diatomic species for such tests.

Methods of evaluating the sense of electric polarity of small molecules from experimental data are poorly developed. The original method involved the isotopic dependence of the rotational $g$ factor, deduced from application of the Zeeman effect to molecules either in a conventional microwave spectrometer or in a molecular beam with mass-spectrometric or other detection. During the period between years 1980 and 1995 experiments on the Zeeman effect in microwave spectroscopy seem to have become less common than during the preceding decade or two, contrary to the trend of increasingly numerous scientists in general and microwave spectral experiments in particular. In fact the development of instruments to produce microwave spectra from Fourier transforms of temporal signals has so far generally precluded use of even the Stark effect. Quantum-chemical computations yield directly such polarities. In principle distributions of electronic and nuclear charge determined in experiments with diffraction of xrays also provide this information, but the most commonly practised experiment of this kind requires single crystals of generally pure substances; strong interactions within the lattice thus formally preclude attribution of deduced properties to individual molecules. In these circumstances our development of a further method to evaluate electric dipolar moments and polarities from precise data of spectral frequencies, such as those measured with new microwave spectrometers, is timely and valuable despite that the approach appears to be limited to diatomic and linear triatomic molecular species having sufficient isotopic variants for which precise and abundant pure rotational and vibration-rotational spectral data are obtainable.

Not only is the electric dipolar moment a chemically meaningful molecular property, but also the intensity of the pure rotational spectrum in absorption or emission is proportional to the square of this quantity. Thus nonadiabatic rotational effects, specifically $t_0^{a,b}$ deduced from frequency measurements, provide indirect information about spectral intensities in the pure rotational spectrum, with prospective analytical applications for samples in exotic environments. Further radial coefficients $t_1$, $t_2$ etc. are related to successive derivatives of the electric dipolar moment with respect to internuclear distance, generally evaluated at $R_e$. In principle such information defines intensities of vibration- rotational spectra, $d\mu^e/dR$ for the fundamental band, $d\mu^e/dR$ and $d^2\mu^e/dR^2$ for the first overtone band etc. In practice precise evaluation of radial coefficients $t_j$ beyond $j=0$ becomes increasingly difficult and susceptible to error propagated ultimately from uncertainty of measurements of transition frequencies for spectral data of finite extent of a particular compound, even with abundant isotopic variants; separation of adiabatic, nonadiabatic rotational and nonadiabatic vibrational effects also becomes increasingly difficult. As table 1 demonstrates, nonadiabatic vibrational effects vanish identically by cancellation for term coefficients $Z_{0,l}$ with $l > 0$; there is thus no interference from nonadiabatic vibrational effects in the evaluation of radial coefficients $t_0^{a,b}$ that are derived primarily from $Z^r_{0,1}$. Radial coefficients $s_0^{a,b}$ are also expected to provide information about the derivative of electric dipolar moment with respect to internuclear distance; models for pertinent nonadiabatic vibrational effects and their quantal justification are in course of development.

The model according to which a diatomic molecule consists of two atomic centres, which become neutral atoms or atomic ions in the event of dissociation, has a sound physical foundation established on data from experiments on diffraction of electrons and xrays. What is the physical foundation of a model of a diatomic molecule as a rotating electric dipole? Certainly diatomic molecules with nuclei having unlike protonic numbers generally possess electric dipolar moments (defined with respect to the nuclear frame). A static spatial distribution of positive and negative electric charges, or the mean field of electrons moving relative to atomic nuclei, can be expressed as a multipole expansion. After the net charge of the monopole, which vanishes for a net electrically neutral molecule, the dipolar moment is the next term in the expansion. If the spatial distribution is not static but varies temporally in an oscillatory manner, the dipole becomes a vibrating dipole; if the entire distribution of charges rotates about an internal origin, the dipole becomes analogously a rotating electric dipole, possibly generating a magnetic dipolar moment in the process. In either case interaction of a vibrating or rotating dipole with an electromagnetic wave provides classically a mechanism for absorption or emission of energy by the molecule. Thus although a diatomic molecule is not merely a rotating or vibrating electric dipole, electric dipolar moment is an important property of such a molecule; the model of a diatomic molecule as a rotating electric dipole that we employ here to evaluate electric and magnetic properties has thus a rational physical basis. A quantal treatment that justifies this model is currently under development.

In conclusion the models of a diatomic molecule to consist of two atomic centres strongly interacting and of a rotating electric dipole are shown not only to yield valuable information about structural, dynamic, electric and magnetic properties from analysis of molecular spectra but also to have a firm physical foundation consistent with traditional ideas about molecular structure. Structural ($R_e$ and coefficients of the expansion for potential energy) and dynamic (force coefficient $k_e$, reflecting the resistance of the molecule to a small displacement from the equilibrium internuclear distance) information may be evaluated highly precisely, to the extent of parts in $10^6$ (including uncertainties in fundamental physical constants $h$ and $N_A$), whereas electric and magnetic properties deduced from extra-mechanical effects are necessarily much less precise because of their origin in secondary effects present to a minor extent (for vibrational states at energies far from the relevant limit of dissociation). Signs of electric dipolar moment and rotational $g$ factor deduced directly according to this approach provide information not readily obtained otherwise.

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