Theoretical investigation of the hyperfine structure in spatially and spin degenerate electronic states of triatomic and tetra-atomic molecules

STANKA JEROSIMIĆ*, MARIJA KRMAR, JELENA RADIĆ-PERIĆ# and MILJENKO PERIĆ

Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12, 11000 Belgrade, Serbia and Montenegro

(Received 2 December 2004)

Abstract: The present paper reviews the results of ab initio studies on the magnetic hyperfine structure in spectra of spatially and spin degenerate electronic states of triatomic and tetra-atomic molecules. The main goal of the present paper is to show that such theoretical investigations can be used to reliably reproduce, explain and predict the results of the corresponding measurements.

Keywords: Ab initio calculations, magnetic, hyperfine coupling, Renner–Teller effect, triatomic and tetra-atomic molecules.

CONTENTS

1. Introduction
2. Hyperfine structure of multiplet electronic states exhibiting the Renner–Teller effect
3. Examples
   3.1. HN3
   3.2. H2O+
   3.3. BH2
   3.4. HCO
   3.5. C2H
   3.6. CCCH
   3.7. HCCS
4. Conclusions

INTRODUCTION

For a long time experimental, particularly spectroscopic investigations have been the only source of information about the molecular structure. This is quite understandable, because the discovery of the laws of nature governing the behavior

* Corresponding author.
# Serbian Chemical Society active member.
of molecules (quantum mechanics) is much younger than the origin of experimental spectroscopy. But even after these laws had become known, one have had to wait quite a long before it has become possible to employ this knowledge to solve concrete molecular problems. The situation has changed, however, in last several decades in which theoretical investigations, particularly ab initio calculations, have become almost as important source of information about the molecular structure as their experimental counterparts.

Although the ab initio method is commonly defined as an exact approach based solely on the first principles of quantum mechanics, which does not build on any a priori knowledge of the system considered (except for elementary data involving the number of electrons and the masses and charges of the nuclei), its actual application is generally connected with a number of specific approximations which role is to reduce the computational requirements. However, these approximations are physically well justified, and in contrast to the situation with so called semi-empirical approaches, easily controlled; if necessary, they can be removed whenever their reliability is questionable. The general strategy is guided by experience gained in experimental spectroscopy, namely that molecular spectra can be, at least in the first approximation, well understood as superposition of effects arising by several degrees of freedom loosely coupled with one another. Translated into the language of quantum mechanics, the philosophy is the following one: The exact Schrödinger equation for a molecule with \( N \) electrons and \( S \) nuclei involves \( 3N \) electronic space- and \( N \) spin-coordinates, and \( 3S \) space- and \( S \) spin- coordinates of the nuclei. Since a partial differential equation of that order cannot be solved in a reasonable time with sufficient accuracy either analytically or numerically for any but the simplest atomic and molecular species, the first step consists in looking for the way to represent the molecular Hamiltonian in the form

\[
H = H_0 + H',
\]

where \( H_0 \) is the leading part of the Hamiltonian, expressible as a sum of mutually independent terms, and \( H' \) involves the terms which spoil the separaton of the variables. Ideally, the operator \( H_0 \) were of the form

\[
H_0 = H_e + H_\Omega + H_r + H_{es} + H_{ns},
\]

where \( H_e \) represents the electrons, \( H_\Omega \) vibration, \( H_r \) rotation, \( H_{es} \) electron-spin and \( H_{ns} \) nuclear-spin Hamiltonian (translations are assumed to be separated off). However, in spite of the fact that the ansatz (2) is in accordance with the theoretically predicted and experimentally proven hierarchy of energetic effects, differing generally from one another by several orders of magnitude, the separation of variables cannot proceed directly in this way. The reason for that is that some of the degrees of freedom are intimately correlated with one another, as for example the spatial and spin electronic (or nuclear) coordinates due to constrains following from the
Pauli principle. Thus the zeroth-order molecular Hamiltonian is usually assumed in the form not involving the spin variables (non-relativistic approximation), i.e.,

\[ H_0 = H_e + H_{0} + H_r \]  

(3)

On the other hand, the spin coordinates are incorporated in the properly symmetrized wave functions. The eigenfunctions of \( H_0 \) (3) are given by

\[ \Phi_0 = \Phi_e \Phi_0 \Phi_r, \]  

(4)

where \( \Phi_e \), \( \Phi_0 \) and \( \Phi_r \) represent the solutions of the eigenvalue problems

\[ H_e \Phi_e = E_e \Phi_e, \quad H_0 \Phi_0 = E_0 \Phi_0, \quad H_r \Phi_r = E_r \Phi_r. \]  

(5)

The corresponding eigenvalues of the Hamiltonian \( H_0 \) are

\[ E_0 = E_e + E_0 + E_r \]  

(6)

Eq. (6) represents the ansatz widely used in molecular spectroscopy. The eigenvalues and eigenfunctions of \( H_0 \) represent a good approximation to the eigenvalues and functions of the total molecular Hamiltonian if \( H_r \) is really small part of \( H \). If higher accuracy is desired, one can construct and subsequently diagonalize the matrix of the complete Hamiltonian in the basis consisting of products of \( \Phi^i_e \Phi^j_0 \Phi^k_r \), where superscript \( i \) labels different eigenfunctions of the electronic operator \( H_e \), superscript \( j \) those of \( H_0 \), and \( k \) the eigenfunctions of \( H_r \).

Alternatively, the contribution of the coupling can be taken into account employing perturbative techniques.

In the early phase of quantum mechanical molecular calculations the quantities have been computed which generally cannot be directly compared to measurements, for example equilibrium geometry parameters, vertical electronic transition energies and potential energy surfaces. The bridge between these quantities and the results of experimental have succeeded in extracting from their measurements the quantities resulting from quantum mechanical structure calculations. On the other hand, theoreticians have developed approaches for calculating rovibrational structure of spectra employing the computed potential surfaces. With the improvement in the accuracy of these surfaces is has become realistic to include continuously finer effects [vibration-electron (vibronic) and spin-orbit (S–O) coupling, hyperfine (hf) interactions] into the theoretical treatment, which then allows for construction of a molecular spectrum in all its details.

The goal of this paper is to review the results of ab initio investigations of the magnetic hf structure of molecular spectra, carried out by the present authors and their colleagues. Energetic effects caused by the nuclear magnetic interactions are several orders of magnitude smaller than even those resulting from the S-O coupling. That means that the corresponding terms in the molecular Hamiltonian are negligibly small compared to those appearing on the right-hand side of Eq. (3).
the other hand, the \( hf \) splitting of spectral lines can be measured precisely and gives important information about the molecular structure. These facts determine the strategy of an \textit{ab initio} handing of the \( hf \) effects: In calculations of global wave functions the term of the Hamiltonian describing \( hf \) interactions is neglected; the energetic effects caused by the nuclear magnetic interactions are taken into account by averaging this part of the Hamiltonian over the wave function for a particular rotational-vibrational-electronic (rovibronic) level.

The molecular systems considered in the present study, namely triatomic and tetra-atomic molecules in (generally) non-singlet spatially degenerate (at linear nuclear geometry) electronic states belong to those for which almost all simplifications applied in usual \textit{ab initio} computations have to be abandoned: This concerns first the application of the non-relativistic and the Born–Oppenheimer\(^1\) (B–O) approximaton, serving to separate the spatial and spin coordinates, and the electronic and nuclear degrees of freedom from one another. A reliable computation of the \( hf \) coupling constants (\( hfcc-s \)) requires a handling of the electronic Schrödinger equation beyond the effectively one-electron Hartree–Fock (H–F) approach. Furthermore, the coupling between the bending vibrational and the rotational motions (at least) around the axis corresponding to the smallest moment of inertia (\( z \)) cannot be neglected. In this paper we refrain from presenting the underlying theory; instead we refer to the original and review papers\(^2\)\textsuperscript{11} where it is presented in detail. We restrict ourselves to the concrete examples which show how theoretical investigations can help to interpret and predict the \( hf \) structure of electronic spectra in such complex systems.

2. HYPERFINE STRUCTURE OF MULTIPLET ELECTRONIC STATES EXHIBITING THE RENNER–TELLER EFFECT

All system considered in the present paper belong to those which electronic state is spatially degenerate at the linear nuclear arrangement (\( \Pi, \Delta, ... \)), exhibiting thus the so called Renner–Teller (R–T) effect\(^12\). The R–T effect in triatomic molecules is one of the most usual examples for the break-down of the Born–Oppenheimer approximation. Since at bent nuclear arrangements one has two close-lying electronic states (we denote them by 1 and 2), which correlate with a degenerate \( \Pi, \Delta, ... \) species of the linear molecule, the usual B–O model, according to which the total molecular wave function (\( \Psi \)) is written in form of the product of an electronic (\( \psi \)) and a nuclear function (\( \Phi \)), has to be generalized:

\[
\Psi = \psi_1 \Phi_1 + \psi_2 \Phi_2. \tag{7}
\]

Experimentally, the R–T effect manifests itself in a complex irregular structure of the electronic spectra. The situation is additionally complicated by the presence of the spin–orbit coupling, being a consequence of the fact that the electronic states in question are in majority of cases also spin degenerate. Both of the coupling mentioned above have a significant effect on the hyperfine structure of the corresponding spectra.
The microscopic Hamiltonian describing the magnetic hf interaction of the nucleus $N$ with the electrons of the molecule can be written in a form:  

$$H_{hf}(N) = \sum_i \left[ \frac{8}{3} \vec{I}_N \cdot \vec{s}_i d(\vec{r}_{iN}) + \frac{\vec{I}_N \cdot (\vec{r}_{iN} \times \vec{p}_i)}{r_{iN}^3} - \frac{3}{r_{iN}^3} (\vec{r}_{iN} \cdot \vec{I}_N) (\vec{r}_{iN} \cdot \vec{s}_i) \right],$$  

where $g_e$ and $g_N$ are the $g$-factors for the electron and nucleus, respectively, $\mu_B$ and $\mu_N$ the values for the electronic and nuclear magneton, $s_i$ and $I_N$ the spins of the electron $i$ and the nucleus $N$, $p_i$ is the linear momentum of the electron $i$, $r_{iN}$ represents the distance between the electron $i$ and the nucleus $N$, and $\delta(r_{iN})$ is the Dirac $\delta$-function. The sum in Eq. (8) runs over all molecular electrons.

The first term in the expression (8) is the Fermi contact term – it is also called the isotropic hfcc. The second term of (8), containing implicitly the angular momentum of the electrons, gives generally a small contribution to the expectation value of the Hamiltonian (8) and is neglected in the present study. The third and fourth term in (8) can be written together in the form

$$H^{(2)}_{hf}(N) = \sum_i \vec{I}_N \cdot \vec{T}^{(2)}_{hf}(i,N) \vec{s}_i,$$  

where $H^{(2)}_{hf}(N)$ is a traceless reducible second-rank tensor called the anisotropic hf tensor. Rewritten in the phenomenological form, the operator (9) becomes

$$H^{(2)}_{hf}(N) = \vec{S} T_N \vec{I}_N,$$  

where $\vec{S}$ is the total electronic spin of the molecule. We denote the Cartesian components of the tensor $T_N$ by $T^{\eta}_{\xi N}$ with $\eta = x, y, z$. For the sake of simplicity, in the following text we omit the subscript $N$ denoting the nucleus in question. We shall also use the elements of the tensor $A$ defined by relations

$$A^{(i)}_{\xi \eta} = A_{iso} \delta_{\xi \eta} + T^{(i)}_{\xi \eta},$$  

with $\xi, \eta = x, y, z$, and $A_{iso}$ denoting the Fermi contact term.

In experimental studies, particularly those concerning linear molecules, the elements of the hf tensor are usually given in terms of the parameters, $b, c, d$ and $e$, connected with the above defined quantities by the relations

$$c \equiv \frac{3}{2} (A_{zz} - A_{iso}) \equiv \frac{3}{2} T_{zz}$$  

$$b \equiv A_{iso} - \frac{T_{zz}}{2}$$  

$$d e^{2i\theta} \equiv \frac{1}{2} (A_{zz} - A_{yy} \pm 2iA_{xy}) = \frac{1}{2} (T_{xx} - T_{yy} \pm 2iT_{xy})$$  

$$e e^{i\theta} \equiv A_{zz} \pm iA_{yx}$$  

with $\theta$ being the angle between the $z$-axis and the vector $\vec{A}_{iso}$.
where $\theta$ is the azimuth angle of the electron with respect to the $z$-axis. By writing the formulae (12) we assume that integration of the $hf$ Hamiltonian over the electronic coordinates is carried out. In the present paper we shall call the electronic matrix elements of the quantities appearing in Eqs. (12) the electronic $hfcc$-s, in order to distinguish them from their counterparts obtained after subsequent integration over the vibration coordinates – the latter species will be called vibronic $hfcc$-s.

On a number of examples (see, e.g., Refs. 4–10) it has been shown that a reliable interpretation and prediction of the experimentally derived values for $hfcc$-s can in general be achieved only in highly sophisticated $ab initio$ calculations. This concerns first the computation of electronic $hfcs$-s. One requires normally better atomic orbital basis sets in H–F calculations (assumed to be carried out via Roothaan’s MOLCAO scheme) than in computations of the potential surfaces and related molecular properties. Accurate values for isotropic $hfcc$-s can be computed only by means of the approaches which properly describe the electron correlation. On the other hand, reliable components of the anisotropic part of the $hf$ tensor can frequently be obtained already in the H–F calculations.

It has been found that the agreement between the results of $ab initio$ calculations for $hfcc$-s and the corresponding experimental findings (at least for the systems considered in the present study) cannot in general be achieved without a proper averaging of the electronic $hfcc$-s over the vibronic wave functions. The change of the vibronic $hfcc$-s from one vibronic level to another reflects generally three interrelated effects: $a)$ geometry dependence of the electronic $hfcc$-s; $b)$ composition of the vibronic wave function, particularly the amount of mixing of the electronic states; $c)$ strong local coupling between (accidentally) close-lying vibronic species, belonging in the zeroth-order approximation (i.e., when the vibronic and S–O couplings are neglected) to different electronic states. The last two effect are obviously intimately connected with each other, because near degeneracy of interacting vibronic levels has a dramatic effect on the composition of the corresponding wave functions.

Experimental determination of the $hfcc$-s is a difficult and expensive task. It requires the use of effective Hamiltonians which incorporate besides the magnetic $hf$ effects also all other kinds of couplings. Furthermore, the current experimental techniques do not enable extracting all components of the $hf$ tensor, and very frequently it is not possible to understand the reasons for variations of $hfcc$-s from one level to another alone on the basis of experimental findings. The above difficulties are not present in a theoretical determination of $hfcc$-s. All components of the $hf$ tensor can routinely be computed and the $ab initio$ calculations, carried out at a sufficiently high level of sophistication give in general a clear insight into the mechanisms governing all aspects of the behavior of the $hfcc$-s. A serious disadvantage of theoretical handlings of the problem in question is generally lower accuracy of the quantities computed in comparison with their counterparts derived from high-resolution spectroscopic measurements.
3. EXAMPLES

3.1. NH$_2$

The NH$_2$ radical in its two lowest-lying electronic states, X$^2$B$_1$ and A$^2$A$_1$, correlating at the linear geometry with the $1^2\Pi_0$ species, represents a classical example for the appearance of the R–T effect. The R–T effect was experimentally evidenced for the first time in the spectrum of this molecule,$^{15}$ twenty five years after it had been theoretically foreseen.$^{12}$ It was stated, however, that NH$_2$ has a strongly bent equilibrium geometry in its ground electronic state X$^2$B$_1$ (equilibrium bond angle value of 103 degree), while in the A$^2$A$_1$ it is quasilinear with the valence angle of about 144 degree.$^{16, 17}$ This system has been subject of extensive ab initio calculations by one of the present authors.$^{18, 2}$ The potential surfaces for NH$_2$ were also derived by Jungen et al.$^{19}$ on the basis of the measured positions of spectral lines. The last fact made possible to investigate the effect of restricted accuracy of the ab initio computed potentials on the results for vibronic hfcc-s.$^{20,21}$ This matter was analyzed in detail in Ref. 4. In the present paper the comparison between the results of our computations and the available experimental findings for the lowest-lying vibronic level$^{22–28}$ is shown (Table I). Theoretical predictions for other levels can be found in original Refs. 20, 21.

The ab initio calculations showed that the variation of the isotropic hfcc-s for both nitrogen and hydrogen atoms is much less pronounced in the electronic state X$^2$B$_1$, which wave function is perpendicular to the molecular plane, than in the in-plane state A$^2$A$_1$. At linear molecular geometry the electronic isotropic hfcc for $^{14}$N and H were computed to be 44 and $-77$ MHz, respectively. At the equilibrium geometry of the ground electronic state the corresponding values are 22 and $-62$ MHz, while in the A$^2$A$_1$ state at its equilibrium geometry they were found to be 104 ($^{14}$N) and 12 (H) MHz. This situation is typical for majority of the systems considered in the present study. The molecular geometry dependence of the components of the anisotropic hf tensor is in general less pronounced but depends on choice of the coordinate system in which they are presented. The experimentalists give, namely, their results most frequently in two coordinate systems: If the values for the hfcc-s are extracted from measurements in the solid phase, the anisotropic hfcc-s are normally expressed with respect to the principal axis system of the hf tensor; on the other hand, the results of the gas phase measurements are generally presented in the system of principal moments of inertia ($a$, $b$, $c$). The results presented in Table I correspond to the latter choice. The theoretical results denoted by th. 1 correspond to the use of the experimentally derived potential energy surfaces.$^{19}$ combined with ab initio calculated hfcc-s, while th. 2 denotes pure ab initio results. Note that the discrepancies between both sets of results are in most cases insignificant in comparison to the differences between the theoretical and experimental values, as well as between the results of different experimental studies) thus justifying
TABLE I. Comparison of the results of *ab initio* study\textsuperscript{21} for vibronically averaged *hfcc*-*si* of the lowest-lying vibronic level of the *X^2B_1* state of NH$_2$ with the corresponding experimental data

<table>
<thead>
<tr>
<th></th>
<th>NH$_2$</th>
<th></th>
<th>NHD</th>
<th></th>
<th>ND$_2$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>th. I</td>
<td>22.4</td>
<td>-62.2</td>
<td>22.4</td>
<td>-62.2</td>
<td>-9.55</td>
<td>22.3</td>
</tr>
<tr>
<td>th. II</td>
<td>22.5</td>
<td>-62.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$A_{\text{iso}}$\textsuperscript{a} = 27.9(0.6)\textsuperscript{a} 

(MHz) exp. $28.2\pm0.4$\textsuperscript{b} $-67.2$\textsuperscript{c} $-10.3$\textsuperscript{c} $-10.1(3)$\textsuperscript{f} 

$A_{\text{aa}}$\textsuperscript{a} = $43.3(1.5)$\textsuperscript{a} 

(MHz) exp. $42.8\pm1.3$\textsuperscript{b} $18.6\pm1.3$\textsuperscript{b} $-43.13(48)$\textsuperscript{g} $-2.3$\textsuperscript{f*} 

$A_{\text{bb}}$\textsuperscript{a} = $44.2(1.6)$\textsuperscript{a} 

(MHz) exp. $44.7\pm1.0$\textsuperscript{b} $-13.4\pm0.9$\textsuperscript{b} $-44.27(63)$\textsuperscript{g} $-2.108(69)$\textsuperscript{g} 

$A_{\text{cc}}$\textsuperscript{a} = $87.4(0.9)$\textsuperscript{b} 

(MHz) exp. $87.5\pm0.5$\textsuperscript{b} $-5.2\pm0.6$\textsuperscript{b} $87.4138$\textsuperscript{e*} $-0.766$\textsuperscript{e*} 

$A_{\text{ab, th. I}}$ = 55.3 

(MHz) exp. $58.5(2.5)$\textsuperscript{c+} 

th. I: Theoretical results obtained by using the potential of Jungen *et al.*\textsuperscript{19} th. II: Pure *ab initio* results. a = Ref. 22; b = 23; c = 24; d = 25; e = 26; f = 27; g = 28; Values in parentheses denote third standard deviations and apply to the last digits of the constants. Expositions are data from Refs. f (1 standard deviation) and c (95% confidence limit). * denotes values obtained from the published data using the relation $A_{\text{bb}} + A_{\text{cc}} = -A_{\text{aa}}$ Obtained indirectly by comparing the values for $A_{\text{aa}}$ and $A_{\text{bb}}$ in NH$_2$ and NHD.
the reliability of the *ab initio* computed potential surfaces. The degree of agreement between the theoretical and experimental results shown in Table I should be comprehended as typical for the time they were produced.

The vibronic levels which correspond to the value $K = 0$ for the projection of the total angular momentum of the molecule, excluding spin, on the $z$ axis ($= a$) are unambiguously attributed to either one of the two electronic states in question and in this case the change of vibronic $hfcc$-s from one level to another is caused predominantly by the geometry variation of the corresponding electronic $hfcc$-s. As seen from Table I the vibronic averaging has insignificant effect on the isotropic $hfcc$-s in the lowest-lying ($K = 0$) vibronic level of the ground electronic state. The situation is completely different for the $K \neq 0$ levels, particularly in the vicinity of the barrier to linearity, where these levels are more or less shared between both electronic states and the change in vibronic $hfcc$-s reflects also the amount of mixing of the wave functions corresponding to these electronic species. This is reflected in erratic dependence of the vibronic $hfcc$-s on the bending quantum number. For details concerning this matter the reader is referred to the original papers 20 and 21.

3.2. $H_2O^+$

The molecular ion $H_2O^+$ is isoelectronic with $NH_2$ and has the same pair of the lowest-lying electronic states, $X^2B_1$ and $A^2A_1$, which correlate with the $1^2\Sigma_u$ species at the linear geometry. However, while the ground state has a similar equilibrium geometry as its $NH_2$ counterpart, in the upper state $H_2O^+$ is linear. The results of an *ab initio* study on the vibronic 30 and magnetic hyperfine structure 31 of this system resolved some controversies concerning the spectrum of this ion. 19 The *ab initio* computed isotropic and anisotropic $hfcc$-s turned out to be in a very reasonable agreement with the experimentally derived results. 32, 33

3.3. $BH_2$

Two lowest-lying electronic states of the $BH_2$ radical build also a $R–T$ pair, $2\Pi_u(X^2A_1, A^2B_1)$. In the ground electronic state, $X^2A_1$, the equilibrium geometry of the molecule is slightly bend (bond angle of about 130 degree), while it is linear in the excited state. Note that the ordering of the states is inverted with respect to those of $NH_2$. Because of a more pronounced quasilinear character of the $2\Pi_u(X^2A_1, A^2B_1)$ system of $BH_2$ vibronic averaging plays an important role already in the lowest vibronic state. It was found that in this case the influence of the stretching vibrations on the final results for $hfcc$-s has also to be taken into account. The *ab initio* computed value for the isotropic $hfcc$ for boron ($^{11}B$) was $345$ MHz, 34 being in reasonable agreement with the corresponding experimental finding of $358$ MHz. 35 For the hydrogen atom the *ab initio* value is $35$ MHz, while the experimentally derived results is $38$ MHz.
3.4. HCO

In both of its lowest-lying electronic states X^2A', A^2A'' (1^2Π at the linear geometry) the HCO radical has non-linear equilibrium geometry. The hyperfine structure of this system has been the subject of numerous experimental investigations.\textsuperscript{36-45} It was calculated in Ref. 46. While the electronic hfcc-s computed for \textsuperscript{13}C and \textsuperscript{17}O agreed reasonably with the corresponding experimental results, in turned out that vibronic averaging played a dramatic role in the case of hydrogen atom. So e.g., the electronic mean value for the isotropic hfcc of H in the lowest-lying vibrational level of the ground electronic state was corrected by almost 50 MHz after vibronic averaging, which had as a consequence an excellent agreement between the final theoretical results and their experimentally derived counterparts. The prime course for importance of the vibronic averaging is in this case not the vibronic coupling of the electronic states in question, because the ground vibrational state lies in the energy region far away from the barrier to linearity, but extremely strong geometry dependence of the electronic hfcc for H, accompanied by a very pronounced anharmonicity of the potential surface for the ground electronic state.

3.5. C\textsubscript{2}H

The C\textsubscript{2}H radical has been the favorite molecule for one of the authors of the present paper. It was the subject of a series of both theoretical and experimental studies carried out at the Bonn University.\textsuperscript{47–56} This species of great astrophysical/chemical relevance and an important intermediate in numerous reactions in laboratory has three close-lying electronic states, X^2Σ\textsuperscript{+}, A^2Π(2^2A', 2^2A''), all of them interacting with one another via different mechanisms. The complexity of the C\textsubscript{2}H spectrum is caused by a) vibronic interaction of all three electronic states including a generalized R–T effect: b) strong coupling between the (large-amplitude) bending and the C–C stretching mode; c) S–O interaction; d) magnetic hf interaction. We do not want to go into details of the structure of spectra involving the electronic states in question, and refer instead to the original studies cited. We restrict ourselves only to two details concerning the hf effects.

Cohran et al.\textsuperscript{57} found that the ratio of the splitting of the lines in the electron spin resonance spectra of C\textsubscript{2}H and C\textsubscript{2}D attributed to the hf structure of the hydrogen isotopes is 6.33, differing significantly from the theoretically expected value of 6.51. The authors concluded that “the mechanism which produces the observed hyperfine splitting in ethynyl is rather complicated, and at present we cannot explained this isotope effect”. The result of the theoretical study (Ref. 52), 6.32, was in quantitative agreement with this finding and moreover offered its simple explanation: in C\textsubscript{2}D the ground vibronic level lies somewhat lower than in C\textsubscript{2}H and consequently possess a slightly smaller admixture of the Π electronic species lying roughly 3500 cm\textsuperscript{-1} above the ground X^2Σ\textsuperscript{+} state at the equilibrium geometry of the latter (6 vs. 7%). Since according to the \textit{ab initio} calculations the electronic hfcc for the Σ\textsuperscript{+} state has the value of 45 MHz, and that for the Π state is −43 MHz, it follows that the vibronic hfcc in C\textsubscript{2}D should slightly increase relative to that in C\textsubscript{2}H.
Note that the correct number, 6.32, can be obtained per hand if the above quoted contribution of the II state and the values for the electronic hfcc are known.

Woodward et al.\textsuperscript{58} found that in the (010) $K = 1$ vibronic state of $\text{C}_2\text{H}$ the dipole-dipole parameter $c$ is 7\% larger than in the ground state; but the Fermi contact parameter, $b_F$, is 21\% smaller, possibly reflecting the effect of vibronic mixing of the unpaired electron. The study (Ref. 52) predicted almost exactly the same decrease of the $b_F$ value by going from (000) to (010) vibronic level (39.26 and 31.84 MHz, respectively) and very similar ($\approx$ 5\%) increase of $c$, both of these effects being easily explainable in terms of a significant stronger admixture of the II electronic state in the (010) vibronic species, and of the values of the isotropic $htcc$ and the $A_{zz}$ component of the anisotropic $hf$ tensor.

3.6. CCCH

First evidence of the R–T effect in a tetra-atomic molecule was reported by Herzberg in 1963.\textsuperscript{59} Contrary to the situation with triatomics, in this case the experiment preceded the theory (Petelin and Kislev\textsuperscript{60}). Herzberg’s observation concerned two Rydberg state of acetylene, investigated later in detail by Colin and Herman.\textsuperscript{61} The theory of the R–T effect in tetra-atomic molecules is much more complicated than in triatomics, because of two bending modes causing the vibronic coupling. The approach by Petelin and Kiselev was modified and generalized by one of us and his colleagues.\textsuperscript{62–69, 5–8, 11}

For a long time after Herzberg’s observation the experimental information on the R–T effect in tetra-atomic molecules has been scarce. The situation has changed, however, in the last decade in which a series of experimental studies on the Rydberg states of acetylene and the ground states of $\text{C}_2\text{H}_2^+$, $\text{HCCO}$, $\text{HCCS}$ and

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{CCC–H (left-hand side) and C–CCH (right) bending potential curves for components of the $\chi^2II$ electronic state of CCCH. On the abscissa the supplements of the corresponding bond angles are presented.}
\end{figure}
CCCH have been published (for the literature survey the reader is referred to the reviews 6 and 8). In the present paper we discuss briefly only two examples.

The CCCH radical is supposed to be a key molecule in the carbon-chain growth in the interstellar medium. It has been observed both in space and laboratory. Its X^2Π electronic state has been investigated by means of an ab initio approach in Refs. 74–77. The most spectacular features of the spectrum of CCCH are that the first excited vibronic level was found to lie only 28 cm⁻¹ above the ground vibronic level, in spite of the fact that the values for the bending vibration frequencies were estimated to be \( \omega_d = 600 \text{ cm}^{-1} \) (CCC–H bending) and \( \omega_5 = 300 \text{ cm}^{-1} \) (CCH bending),78 and that the computed value for the S–O coupling constant79 was roughly twice as large as the measured S–O splitting in the lowest vibronic level.72, 80 Both of these peculiarities were reproduced reliably in our previous ab initio study74; it was shown that they are a consequence of the extremely flat CCC–H bending potential curve for the lower component of the X^2Π electronic state and thus of a very large value for the corresponding Renner-parameter \( e_4 \).12

The potential energy curves for the CCC–H and the C–CCH bending vibration in the A' and A'' components of the ground electronic state, X^2Π of CCCH are displayed in Fig. 1.74 The behavior of the electronic isotropic hfcc-s upon bending is shown in Fig. 2.75 In order to distinguish between three carbon nuclei we use the notation C_1C_2C_3H. The results for the components of the anisotropic hf tensor are given in Ref. 77.

The generally strong geometry dependence of the electronic hfcc-s presented in Fig. 2, particularly at the CCC–H bending vibrations, indicates unambiguously that a reliable comparison between the theoretical and experimental results cannot be achieved without proper vibronic averaging of these quantities. Such a situation is in general typical for all systems considered in the present study.

![Fig. 2. Bending dependence of electronic A_{iso} for H, ^13C_1, ^13C_2, and ^13C_3 in components of the X^2Π electronic state of C_1 C_2 C_3 H. Full lines: in the A' component; dashed lines: in the A'' state. On the abscissa the supplements of the corresponding bond angles are presented.](image)
The hyperfine structure of the X2Π electronic state of various isotopomers of CCCH, involving all possible combination of 12C, 13C, H and D was calculated in Refs. 75–77. The comparison with the corresponding experimental findings is presented in Tables II (for the ground vibronic level, 2Πg) and III (first excited vibronic level, ν42Σμ). Two sets of theoretical results are given. The first one (th. 1) represents the electronic hfcc-s computed at the linear (equilibrium) nuclear arrangement. The second set (th. 2) includes the results of vibronic averaging of all quantities in question. We do not find it necessary to comment the details of the content of Tables II and III, because it clearly shows how important the vibronic averaging is. Compare, for example, the values for isotropic hfcc-s of 13C3 and H. The overall agreement between all theoretical results (th. 2) and the corresponding experimental findings convinced us that the only exception, namely the anisotropic hfcc-s of 13C3 should be ascribed to the error made by extracton of the quantities in question from the results of measurements.

### Table II. Comparison of theoretical results with the experimental derived data (in MHz) for the hf coupling parameters of the ground vibronic level in the X2Π electronic state of CCCH, th. 1: Electronic hfcc-s. th. 2: Results obtained after vibronic averaging

<table>
<thead>
<tr>
<th></th>
<th>Aiso</th>
<th>b = A1</th>
<th>C</th>
<th>d</th>
<th>Aμ = b + c</th>
</tr>
</thead>
<tbody>
<tr>
<td>13C1 th. 1</td>
<td>33.0</td>
<td>61.2</td>
<td>-84.5</td>
<td>173.3</td>
<td>-23.3</td>
</tr>
<tr>
<td>th. 2</td>
<td>30.9</td>
<td>57.1</td>
<td>-78.7</td>
<td>127.5</td>
<td>-21.6</td>
</tr>
<tr>
<td>exp.</td>
<td>35.0</td>
<td>62.0</td>
<td>81</td>
<td>125.9</td>
<td>-19.0</td>
</tr>
<tr>
<td>13C2 th. 1</td>
<td>-52.0</td>
<td>-62.3</td>
<td>30.9</td>
<td>-16.9</td>
<td>-31.4</td>
</tr>
<tr>
<td>th. 2</td>
<td>-40.7</td>
<td>-51.0</td>
<td>30.9</td>
<td>-12.4</td>
<td>-20.1</td>
</tr>
<tr>
<td>exp.</td>
<td>-39.0</td>
<td>-68.3</td>
<td>88</td>
<td>0.0</td>
<td>20.0</td>
</tr>
<tr>
<td>13C3 th. 1</td>
<td>114.5</td>
<td>135.5</td>
<td>-63.1</td>
<td>95.6</td>
<td>72.4</td>
</tr>
<tr>
<td>th. 2</td>
<td>112.0</td>
<td>-75</td>
<td>90.9</td>
<td>62.0</td>
<td></td>
</tr>
<tr>
<td>H th. 1</td>
<td>-13.0</td>
<td>-23.4</td>
<td>31.2</td>
<td>18.9</td>
<td>7.8</td>
</tr>
<tr>
<td>th. 2</td>
<td>-13.8</td>
<td>-23.5</td>
<td>29</td>
<td>15</td>
<td>5.5</td>
</tr>
<tr>
<td>exp.</td>
<td>-13.8</td>
<td>-23.2</td>
<td>28.3</td>
<td>16.2</td>
<td>5.1</td>
</tr>
<tr>
<td>D th. 1</td>
<td>-6.84</td>
<td>-8.72</td>
<td>5.64</td>
<td>3.96</td>
<td>-3.08</td>
</tr>
<tr>
<td>th. 2</td>
<td>-2.55</td>
<td>-4.15</td>
<td>4.79</td>
<td>2.90</td>
<td>0.64</td>
</tr>
<tr>
<td>exp.</td>
<td>-2.05</td>
<td>-3.45</td>
<td>4.21</td>
<td>2.49</td>
<td>0.75</td>
</tr>
</tbody>
</table>

a: Ref. 80; b: Ref. 81; c: Ref. 72; d: Ref. 73; †: The result derived from those explicitly published; |

`: Fixed / assumed value.
TABLE III. Comparison of theoretical results with the experimental derived data (in MHz) for the $hf$ coupling parameters of the $v_d(^3Σ^+_d)$ vibronic level in the $X^2Π$ electronic state of CCCH.

<table>
<thead>
<tr>
<th></th>
<th>$A_{iso}$</th>
<th>$b = A_J$</th>
<th>$C$</th>
<th>$A_{1q} = b + c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}\text{C}_1$</td>
<td>th. 1</td>
<td>33.0</td>
<td>61.2</td>
<td>-84.5</td>
</tr>
<tr>
<td></td>
<td>th. 2</td>
<td>29.5</td>
<td>54.8</td>
<td>-75.9</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>35$a^{+*}$</td>
<td>62.0$^a$</td>
<td>-81$^a^{+*}$</td>
</tr>
<tr>
<td>$^{13}\text{C}_2$</td>
<td>th. 1</td>
<td>-52.0</td>
<td>-62.3</td>
<td>30.9</td>
</tr>
<tr>
<td></td>
<td>th. 2</td>
<td>-33.3</td>
<td>-43.6</td>
<td>30.8</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>-39$a^{+*}$</td>
<td>68.3$^{a+}$</td>
<td>88$^{a+}$</td>
</tr>
<tr>
<td>$^{13}\text{C}_3$</td>
<td>th. 1</td>
<td>43.8</td>
<td>67.6</td>
<td>-71.4</td>
</tr>
<tr>
<td></td>
<td>th. 2</td>
<td>157.9</td>
<td>177.2</td>
<td>-57.9</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>144$a^{+*}$</td>
<td>169.1$^a$</td>
<td>-75$^a^{+*}$</td>
</tr>
<tr>
<td>H</td>
<td>th. 1</td>
<td>-44.5</td>
<td>-56.7</td>
<td>36.7</td>
</tr>
<tr>
<td></td>
<td>th. 2</td>
<td>6.99</td>
<td>-2.50</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>1.4$^{b+}$</td>
<td>-8.1$^b$</td>
<td>28.5$^b$</td>
</tr>
<tr>
<td>D</td>
<td>th. 1</td>
<td>-6.84</td>
<td>-8.72</td>
<td>5.64</td>
</tr>
<tr>
<td></td>
<td>th. 2</td>
<td>0.18</td>
<td>-1.40</td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>exp.</td>
<td>0.22$^{b+}$</td>
<td>-1.24$^b$</td>
<td>4.37$^{b+}$</td>
</tr>
</tbody>
</table>

$^a$: Ref. 80; $^b$: Ref. 81; $^{+*}$: The result derived those explicitly published; $^*$: Fixed / assumed value.

3.7. HCCS

The HCCS radical represents one of the rare examples of tetra-atomic molecules exhibiting the R–T effect in both ground $X^2Π$ electronic state. In Refs. 82 and 83 the results of an ab initio study on the combined effects of vibronic and $S$–$O$ coupling in both of these states were published. These investigations confirmed the analysis of the experimental findings carried out by Tang and Saito$^{84}$ and helped to resolve the controversy concerning the equilibrium geometry in the excited electronic state (see Ref. 85). In two following ab initio studies$^{86,87}$ the $hf$ structure in the ground electronic state was calculated. The derived conclusions are similar to those concerning the analogous spectral system in CCCH.

4. CONCLUSIONS

In the present study we give a review of the results of ab initio handlings of the magnetic $hf$ effects in spatially and spin degenerate electronic states of several triatomic and tetra-atomic molecules. The results explicitly presented in this paper concern only the cases where a comparison with the corresponding experimental
findings was possible. For a number of predictions concerning the higher-energy vibronic levels, being even more interesting from the theoretical point of view, the reader is referred to the original studies cited. The main goal of the present review is to demonstrate the capability of \textit{ab initio} computations, carried out at a proper level of sophistication, to reproduce, explain and predict the results of corresponding measurements.

\textit{Acknowledgements}: The authors wish to thank all colleagues who have taken part on the calculations presented in this paper. The financial support of the Serbian Ministry for Science is gratefully acknowledged.

\begin{thebibliography}{99}
  \bibitem{1} M. Born, R. Oppenheimer, \textit{Ann. Phys.} \textbf{84} (1927) 457
  \bibitem{12} R. Renner, \textit{Z. Phys.} \textbf{92} (1934) 172
  \bibitem{13} W. Weltner, Jr., \textit{Magnetic Atoms and Molecules}, Scientific and Academic Editions, Van Nostrand Reinhold Company Inc., 1983
  \bibitem{14} C. C. J. Roothaan, \textit{Rev. Mod. Phys.} \textbf{23} (1951) 69
  \bibitem{15} K. Dressler, D. A. Ramsay, \textit{Phil. Trans. R. Soc.} \textbf{A251} (1959) 553
\end{thebibliography}