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REGULAR ARTICLE

Anharmonic treatment of vibrational resonance polyads—the diborane: a critical case for numerical methods

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Abstract Based on accurate computational results, the IR spectra of diborane B_2H_6 and its deuterated derivative B_2D_6 were experimentally revisited to reconsider or complete their band assignments. A pure, variational approach, developed in both mechanical and electrical anharmonicities, was applied to study the diborane molecule for which many uncertainties remain in the spectral IR assignment. This work, together with all the experiments on this system over recent decades, shows the difficulty of interpreting the spectral data, making it a "benchmark" ideal for testing the mathematical approaches for the implementation of vibrational codes.

Keywords Resolution of the vibrational Schrödinger equation · Variational approach · Mechanical and electrical anharmonicities · Diborane · Resonance polyads

1 Introduction

Among the various theoretical challenges encountered in the field of modern vibrational spectroscopy, the need for adequate and accurate descriptions of resonant vibrational states has persistently remained a major challenge for a long time [1–6]. Indeed, without a good understanding or accurate descriptions of fine resonant states, some spectral assignments can be seriously misleading and the interpretations ambiguous. Of course, the experimentalists did not rely on the joint progress in theoretical and computational chemistry to predict, explain, or take into explicit account the couplings between predominant vibrational resonant states. These models have quickly become a mainstay in the spectral function [7–10]. Nevertheless, the difficulty for the spectroscopists lies in how to determine the nature of the couplings so as to correctly assign the vibrational states. These studies, often of very high experimental quality, involve simplified quantitative treatment and parameters that can be described today by *quasi*-variational partial treatment of the vibrational Schrödinger equation (VSE) including anharmonicity effects. Thus, on the basis of simple empirical rules related to the symmetry of normal modes [11, 12], some spectroscopists have shown how it is possible to deduce which vibrational states are potentially coupled. To this rule, one can add a quantitative rule related to the proximity of the energies of the states considered. The description of a given vibrational mode therefore consists of looking for two or three main couplings that allow, with the adjustments based on the experimental observations, to deduce the key cubic and/or quartic(s) force constants involved in the resonance (referred to, in this case, as taking into account the anharmonic part of the VSE). Matrix "representative" of the vibrational Hamiltonian thus obtained gives, after

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diagonalization, a quantitative description of the vibrational modes observed and a qualitative assignment of the "band shift" due to the presence of the highlighted resonance.

These simplified approaches have already shown evidence of a real impact for the interpretation of spectral data from small systems [13–15] or from systems with remarkable features of biological interest. For example [16], the absence of all the secondary couplings in the vibrational Hamiltonian, whose contribution is sometimes non-negligible, and the treatment of the data with empirical adjustments with the weight of the vibrational functions for which the force constants are analyzed with only one coupling considered in the simplified rules outlined above may lead to unfortunate misinterpretations. Even for some small systems for which the interpretations of the experimental data have never been questioned, some doubts are currently resurfacing.

Since the advancement of these semi-quantitative approaches, many methodological developments have emerged. The purpose of this paper is not to identify all existing approaches in this field. It is rather to point out that while the choice of available techniques for solving the VSE has increased, there is nevertheless a major problem common to all these approaches, namely, the need for a reliable and robust description of the resonant states. This article does not therefore pertain to the identification and description of the advantages or disadvantages of all the mathematical approaches. For this, the reader is directed to several major papers in this area [17–24]. The aim of this paper is rather to highlight the drawbacks associated with the use of more or less sophisticated methods, but without prior verification of the impact of the choice on the potential energy surface (PES) and on the resolution vibrational Schrödinger equation (RVSE) in dealing with a non-conventional and complex vibrational problem.

The diborane molecule [25] has been chosen to illustrate a critical resonant situation. First, it is a molecule that still remains controversial when it comes to the allocation of certain overtones and harmonics, but also, more surprisingly, assignment of some fundamental band [26–35]. Secondly, many resonances are present for this system. Thirdly, the dimension of this system is flowless for developing "raw power" interaction configuration (ICs) approaches and/or refined to control the various approximations that can be introduced into the RVSE. Finally, we have all the experimental spectroscopy wavenumbers of absorption bands between 300 and 3,000 cm^{-1}, as well as their intensities for diborane and its deuterated systems. This study is a follow-up of a previous study on the complex of vinylphosphine–borane, where diborane was a reactive precursor. Finally, this work, together with the experiments on this system found for recent decades, shows the difficulty of interpreting the spectral data, making it a critical benchmark for testing the mathematical approaches.

2 Position of the problem

Major theoretical challenges encountered in the "modern" vibrational spectroscopy field are numerous and complex. If we can consider the vitality of a good description of resonant states, it remains as one of many fundamental problems for conducting such studies. One could cite many issues to learn about the various difficulties encountered by theorists in the field of vibrational spectroscopy [36].

In order not to deviate from our main theme and to ease the discussion, we would like to restrict this paper to the treatment of resonant states within the framework of stationary RVSE and the approaches that require the determination of one PES in analytical terms. So, we will focus our discussion on "classical" approaches, based on notions of normal modes and mechanical and electrical anharmonicities.

Methodologically, much progress has recently emerged and helped to provide models that can meet certain expectations set by spectroscopists. One could say that there has been a process of "democratization" of the methods solving the VSE using the hypothesis of mechanical anharmonicity: (1) the perturbation methods [36–38] are probably the most commonly accepted and applied in this area, which, once a partial quartic force field is determined for the description of the PES, solves the VSE with the least CPU cost; (2) both variation or mixed perturbation/variation (p/v) methods are applied for accurate assignments on smallest systems.

If these methodologies were experiencing a renewed interest during the last decade, many problems persist using these approaches especially when the vibrational resonance phenomena are present. These problems are the origins of some of the errors and computational discrepancies. These woes are due to the past theoretical descriptions (besides all the work done with the harmonic assumption that implicitly applied the default of not including a coupling mode). Another error generated during the RVSE process lies in the quality of the force field obtained in our calculations. Indeed, an inappropriate description and approximate energy levels inherent in the PES may cause the occurrence of accidental resonances that can distort the more rigorous devolved approaches to the RVSE. Note that this last point represents the main pitfall of static approaches using an analytical form of the PES.

Another problem concerns the description of floppy modes. This last point is not just specifically relevant to static RVSE/PES methods, but it should be noted that the dynamic methods appear nowadays more efficient in that case (see, in particular, developments on the established Car–Parrinello molecular dynamics (CPMD) methodology, followed by an a posteriori quantization of the stretching motion) [39–42].

Finally, note that all these considerations do not stop at only the RVSE with the hypothesis of mechanical anharmonicity. Taking into account, the electrical anharmonicity encounters similar difficulties related to identification and treatment of the dipole energy surface (DESs). Computational details regarding the calculation of vibrational intensities are available in the literature [43–45].

3 Theory

In this paragraph, both theoretical principles and methods are developed in the context of variational (*v*), perturbational (*p*) and mixed *v*/*p* approaches currently used to the RVSE. In the present case, a working assumption governs this paper: the assumption that is used in our study (always revocable) is that a force field is adapted to the description of a given vibrational problem in order to focus solely on errors related to the RVSE. The reverse situation should, strictly speaking, be treated to show the importance of choosing the set of coordinates, as well as the choice of the analytical form of the PES. However, this work will not be developed in this paper.

3.1 Computational details

Optimized bond lengths and angles calculated for the ground state of B_2H_6 are all reported in Table 1. Our coupled cluster CCSD(T)/cc-pVTZ results, in good agreement with those published by the experimentalists Duncan and Harper [46], are all close to the better level of calculation up till now reported in the literature, that is, MP2/TZ2P + f [34].

Fundamental wavenumbers of B_2H_6 and their isotopic shifts are computed using a hybrid quartic potential in which CCSD(T)/cc-pVTZ equilibrium values and harmonic wavenumbers are coupled to B3LYP/6-31+G** anharmonic terms in the framework of a variational treatment split in several spectral ranges (see details just below) [45, 47, 48]. Two selection criteria are of prime importance in our type of calculation: (1) basis set convergences in CCSD(T) vibrational frequencies, and we encourage readers to analyze previous referenced papers of Gauss, Martin and Stanton et al. [49–51]. (2) The coupling of CCSD(T) quadratic and DFT anharmonic forces constants in order to determine an hybrid PES (see references [52, 53]). So, the quality of the present PES (*V* function) and the computational requirements has already been validated in the study of the vinylphosphine–borane complex [54]. The mean-square deviation between our computed values and the most reliable experimental data is only 0.5% (B_2H_6) and 0.6% (B_2D_6). Calculation of both overtones and combination bands in the medium infrared region suggests a new assignment of some observed bands. Additional intensities calculations computed at B3LYP/6-31+G** level of calculation complete our assignments [45].

3.2 Resonance polyads

In the present work, we are mainly concerned with "2–2" resonance constants (resonances between states that differ by the annihilation of two quanta and the creation of two others), which are related to the Darling–Dennison phenomenon, and the "1–1" resonance (between states that differ by creation and annihilation of only one quantum). This last phenomenon is known as Fermi resonance. Fermi resonance is a purely vibrational perturbation in the sense that the vibrational Hamiltonian is responsible for the interaction between states that are accidentally degenerate. This phenomenon was first recognized in the case of CO_2

Table 1 Structural parameters of B_2H_6

	Experimental	Theoretical			
	Ref. [46]	Ref. [34][a]	Ref. [33][b]	Our work	
	Spectroscopic sources	MP2/TZ2P + *fp*	CCSD/DZP	B3LYP/6-31+G**	CCSD(T)/cc-pVTZ
$r_{BH,\ free}$ (Å)	1.184 (3)	1.1832	1.189	1.190	1.188
r_{BH} (Å)	1.314 (3)	1.3081	1.324	1.316	1.315
r_{BB} (Å)	1.743	1.7483	1.785	1.767	1.763
$\alpha_{(H,\ free)\ BH}$ (deg)	121.5 (5)	122.0	123.0	121.8	122.3
α_{HBH} (deg)	96.9 (5)	96.13	–	95.7	95.8

[a] Harmonic MP2/TZ2P + *f*

[b] Harmonic CCSD/DZP

where the overtone $2\omega_2$ has nearly the same energy as the fundamental ω_1 so that the two levels interact strongly.

3.3 General perturbation theory

If a potential function V is introduced into Schrödinger equation, an exact solution of the type obtained for the harmonic oscillator cannot be found. However, one can take advantage of the fact that for finite but small displacements of the nuclei, the quadratic part of V is much larger than the contribution of cubic terms, which is in turn larger than the quartic part. The vibrational Hamiltonian may thus be divided into orders of magnitude and perturbation theory used to calculate the corrections to the harmonic vibrational energy due to the various terms:

$$V/hc = V^{(0)} + \lambda V^{(1)} + \lambda^2 V^{(2)} + \cdots$$

$$E/hc = \sum_{i=s,t} \omega_i \left(v_i + \frac{d_i}{2} \right) + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots$$

where $V^{(0)} = \frac{1}{2}\sum_{i=s,t} \omega_i q^2_{i,\sigma_i}$, $V^{(1)} = \sum_{ijk=s,t} k_{ijk} q_{i,\sigma_i} q_{j,\sigma_j} q_{k,\sigma_k}$, $V^{(2)} = \sum_{ijkl=s,t} k_{ijkl} q_{i,\sigma_i} q_{j,\sigma_j} q_{k,\sigma_k} q_{l,\sigma_l} \ldots$ and where λ is a parameter defining the order of magnitude of the various terms, the subscripts s and t refer, respectively, to the non-degenerate and doubly degenerate modes and ℓ is the vibrational angular momentum quantum number. The corresponding corrections to the energy to first and second order, respectively, are given by:

$$E^{(1)} = \sum_{v} \langle v, \ell | V^{(1)} | v, \ell \rangle = 0$$

$$E^{(2)} = \sum_{v,\ell} \left[\langle v, \ell | V^{(2)} | v, \ell \rangle + \sum_{\substack{v,\ell \neq v',\ell' \\ v \neq v'}} \frac{\langle v, \ell | V^{(1)} | v', \ell' \rangle \langle v', \ell' | V^{(1)} | v, \ell \rangle}{E^0_v - E^0_{v'}} \right]$$

In these expressions, $\langle v, \ell|$ and $\langle v', \ell'|$ (reduce to $\langle v|$ and $\langle v'|$ from this point) indicate the complete zero-order vibrational wavefunctions corresponding to the vibrational zero-order energies E^0_v and $E^0_{v'}$, respectively. Each matrix element of the vibrational Hamiltonian can be directly evaluated with respect to the vibrational wavefunction. This procedure is easy to implement and has the main advantage of requiring independent matrix element calculations for each vibrational energy level E_v.

While being very efficient, perturbation theory is sensitive to Fermi, Darling-Denisson and other resonances (due, for example, to the presence of the term $E^0_v - E^0_{v'}$ in the denominator). So, adapted solutions have been then developed during the last decades to circumscribe this problem. Let us cite, for example, the contact-transformed vibrational Hamiltonian method coupled with an automatic procedure for setting up and solving the relevant resonance eigensystems of Martin and Taylor [55], the high order canonical Van Vleck perturbation theory [56, 57] and the vibrational self-consistent field (VSCF) approximation, which include corrections for correlations between the modes by perturbation theory developed by Jung and Gerber [58] and Norris [59], that is, correlation corrected VSCF (CC-VSCF).

3.4 Variation theory: brut force (P_VMWCI)

For a more comprehensive treatment of a resonant vibrational spectrum, it is better to use a variational approach. However, there are several well-known difficulties in this method: (1) the amount of data extracted from the potential function V grows dramatically with the size of the molecule; (2) the quality of the method is dramatically dependent on both V quality and the necessity to choose all the N vibrational configurations $S = \left\{ \left| n^i_1, n^i_2, \ldots, n^i_{n_{\mathrm{nvib}}} \right\rangle ; 1 \leq i \leq N \right\}$ coupled with the subspace of the N_0 states $S = \left\{ \left| n^j_1, n^j_2, \ldots, n^j_{n_{\mathrm{nvib}}} \right\rangle ; 1 \leq j \leq N_0 \right\}$ we want to describe. The vibrational solutions sought will be closer to the exact solutions as the base (N) approaches infinity. As the latter always stays finite and limited, the problem lies in the choice of configurations of the space to be diagonalized (N_s). This choice of space to be diagonalized greatly affects the accuracy and speed of convergence of variational methods. Truncating the complete space (N) is becoming the focal point where various approaches with their particular features are currently being developed.

Selection strategies are many and very close to those methods used in quantum chemistry in calculating electron correlation energies. There are almost as many selection strategies as the computer code based on a CI approach. In agreement with both Wyatt et al.'s algorithm [60], the selection of the active space during our CI (P_MWCI) process is based on the use of a wave operator and on an iterative construction of $\langle H_v \rangle$ (cycles). Details are reported in Ref. [48]. So, the configuration space at cycle γ is defined recursively to be the space S_γ, in direct interaction with $S_{\gamma-1}$. The entire problem lies in the choice of active space that is needed to be chosen with the size consistent to the CI process and also the choice of the order of the γ cycle of the truncation that we must inevitably carry out. In any case, a development with $\gamma = 4$ is necessary for the study of weakly resonant state [48] and/or combination or highly excited harmonic modes.

Our choices are not unique. Among other variational developments, let us cite, for example, the pioneering work of Bowman and Gerber concerning the vibrational self-consistent field (VSCF) approach [61–64], MULTIMODE developments [65] and the very efficient approach, the vibrational coupled cluster (VCC) recently developed by Christiansen [18, 66]. More recently, an extension of VSCF by means of *quasi*-degenerate perturbation theory (QDPT) has been developed for an accurate theoretical description of vibrational resonances in polyatomic molecules [15]. The average accuracy of current calculations on small organic systems is now between 1 and 15 cm^{-1} following the nature of the motions studied. This accuracy primarily depends on both the quality and the analytical form chosen for developing force fields. The limitations related to resolution of the VSE are, nowadays, mainly technologic. For medium-size systems, these limitations are now being overcome by developments including highly parallelized software (see P_VMWCI algorithm). We can therefore conclude that these approaches are exact, for systems not exceeding 15 atoms and for a given force field.

3.5 Variant: variation-perturbation and perturbation-change theories

If in the approach of configuration interaction (CI) the choice of the active space is guided by taking into account all the interacting configurations with the system of study $S = \left\{ \left| n_1^j, n_2^j, \ldots, n_{n_\text{nvib}}^j \right\rangle; 1 \le j \le N_0 \right\}$, then the variation-perturbation approaches have been developed to reduce these constraints in order to guarantee, in an iterative process of η iterations, that only the most relevant information be included. The selection of these configurations can be done either on criteria related to the development of the vibrational wavefunction or the energy by calculating the IC process upstream, the energy contribution of all the vibrational states potentially interactive with the active space defined at the $\eta - 1$ iteration by the use of a perturbational method. Once again, there are just as many existing methods as selection choices. Initially, the first variation-perturbation approaches have been developed by selectively choosing the active space by diagonalizing at each iteration and by ranking a few dozens of the vibrational configurations, the weight of the energy of which are the most sensitive to the correction to the wavefunction of the first order. To control the number of iterations, a threshold $\sum$ is initially set by the user to restrict the size of the matrices that are easily diagonalizable. At the end of the iterative process, the weight of the remaining configurations is treated with a second-order perturbational approach. These approaches have shown real impact in terms of numerical accuracy [67–70], but were never really adapted to the calculation of large- and medium-size molecular systems. Very recently, these methods have been revived to study [70] and have been reprogrammed for the first time in the code P_Anharv1.0 (as alternative to the variational crude CI process) and then in VCI-P code.

According to the definitions given above to the variational methods, the variation-perturbation method developed in the code P_Anhar can be defined as:

$$S_\gamma = \left\{ \begin{array}{r} \left| n_1^j, n_2^j, \ldots, n_{n_\text{nvib}}^j \right\rangle \in S; \text{ such that } \exists \left| n_1^i, n_2^i, \ldots, n_{n_\text{nvib}}^i \right\rangle \in S_{\gamma-1} \\ \text{and } \left| \dfrac{\left\langle n_1^j, n_2^j, \ldots, n_{n_\text{nvib}}^j \middle| V^{(1)} \middle| n_1^i, n_2^i, \ldots, n_{n_\text{nvib}}^i \right\rangle}{E_i^0 - E_j^0} \right| > \varepsilon \end{array} \right\}$$

If these approaches are less rigorous, they are an alternative to both the expansion of the problem in terms of size and allow faster processing and selectively direct the main resonant interactions. Their main drawback concerns, however, selectivity. With the risk being to miss vibrational configurations, in the pool of all the vibrational configurations, which are sensitive to a weakly resonant state when interactions are not too strong, these approaches are effective enough to deal comprehensively with or to trim the size of a vibrational problem. They show very quickly when the number of configurations interaction becomes very high. On the other hand, when the description of resonant states is too heavily dependent on the inclusion of indirect interactions, these methods, in general, also fail to adequately describe the fine resonances.

A possible alternative to these variation-perturbation approaches consists of developing perturbation-variation methods. They consist of solving the VSE by using a perturbation approach while seeking potential accidents related to resonance phenomena, both real and artificial. The problem of accidental degeneracies between these resonant states can be fixed by the use of micro-processes involving these variational states. This approach, developed since the first version of the code P_Anhar_v1.0, was originally designed to handle large-sized system. Note that if the criteria related to the selection of resonant states are sufficiently high, the variation-perturbation approach tends to merge with the CI solution of brut force.

When accidental degeneracy occurs between two vibrational levels, it is no longer legitimate to use the perturbation theory in the classical form. The second-order perturbation correction developed in our perturbation-variation approach is then defined as:

$$E^{(2)} = \sum_v \left[\langle v|V^{(2)}|v\rangle + \sum_{j \neq v} \frac{\langle j|V^{(1)}|v\rangle\langle v|V^{(1)}|j\rangle}{E_v^0 - E_j^0} + \sum_{\substack{l \neq v \\ l \neq j}} \frac{\langle l|V^{(1)}|v\rangle\langle v|V^{(1)}|l\rangle}{E_v^0 - \varepsilon_l} \right]$$

with $\sum_1$ resulting from the diagonalization of the micro-spaces:

$$S' = \left\{ \left| n_1^l, n_2^l, \ldots, n_{n_\text{nvib}}^l \right\rangle; l \subseteq \{i\}; 1 \le i \le N \right\}.$$

4 Discussion

4.1 State of the art on diborane

Preparation of diborane and hexadeuterated diborane. Materials: orthophosphoric acid, potassium borohydride, sodium borodeuteride, phosphorus pentoxide and deuterium oxide were purchased from Aldrich and used without further purification.

Diborane (B_2H_6) was prepared as reported in the literature [25]. Orthophosphoric acid (30 mL of 85 wt% in aqueous solution) was introduced into a 500-mL two-necked flask equipped with a stirring bar and a cell containing the potassium borohydride (1.6 g, 29 mmol). The flask was fitted on the vacuum line and degassed for 30 min at 0.1 mbar. The potassium borohydride was slowly added by portions over about 1 h. During and after addition, the formed diborane was distilled off in vacuo from the reaction mixture. A cold trap (−80 °C) selectively removed less volatile products, and the diborane was condensed in a second cold trap (−196 °C). At the end of the reaction, this second cell was disconnected from the vacuum line by stopcocks and kept at 77 K in a liquid nitrogen bath. Yield: 0.25 g, 8.7 mmol of B_2H_6 (60%).

B_2D_6 was prepared starting from a deuterated solution of orthophosphoric acid and sodium borodeuteride using the same experimental procedure. Starting from $NaBD_4$, hydrogenated solvent and reagents, a sample with an about 90% isotopic purity was obtained. Subsequently, only deuterated compounds were used to improve the isotopic purity to more than 98%. The glassware was washed two times with small amounts of D_2O. The deuterated solution of orthophosphoric acid was prepared by the slow addition under nitrogen of P_4O_{10} (28 g, 0.1 mol) by portions to a cooled solution of D_2O (20 g, 1.0 mol). At the end of the addition, the solution was stirred for 10 min at room temperature and used in the synthesis of B_2D_6 without further purification. Thirteen milliliters of this solution and sodium borodeuteride (0.5 g, 12 mmol) were used for the preparation of B_2D_6. Yield: 57%. Isotopic purity ≥ 98%.

Spectroscopic data: The infrared spectra of diborane B_2H_6 and its deuterated derivative B_2D_6 were recorded using a Brucker IFS120HR spectrometer at a resolution of 0.5 cm^{-1}. A 20-cm-long gas cell was used for the acquisition of spectra at different pressures. Two spectral ranges 600–3,500 cm^{-1} and 1,200–6,000 cm^{-1} were investigated using the appropriate detectors (MCT or InSb) and a beam splitter (KBr or CaF_2) combination, which was associated with the use of a Globar infrared source. The pressure was adjusted to 4.8 Torr for the acquisition of fundamental modes of the B_2H_6 spectrum in the first-studied spectral region. It was then increased to 100 Torr in order to enhance the very weak intensities of the combination and overtones absorptions bands, and the acquisition of two spectra, respectively, in the regions 600–3,500 cm^{-1} and 1,200–6,000 cm^{-1} was performed. A set of 100 scans were averaged each time to obtain the final spectrum. The acquisition of the spectrum of deuterated diborane B_2D_6 was necessary to clarify the assignment of combinations bands in certain complex B_2H_6 spectral regions. The infrared spectrum of this deuterated derivative was recorded only in the first-studied spectral region. The acquisitions of two spectra, respectively, at pressures of 1 and 10 Torr were performed. Some bands of fundamental modes of B_2H_6 produce a very resolved rotational structure at resolution of 0.5 cm^{-1} and can complicate the assignment of overtones appearing in the same region. In this case, spectrum of these latters is recalculated at a reduced resolution of 1 cm^{-1}.

Beyond the very well-known bands such as $\sigma_{BH_2,\mathrm{free}}$ (B_{3u}), $\nu_{as,\mathrm{BH}}$ (B_{3u}), $\nu_{s,\mathrm{BH}}$ (B_{3u}) and $\nu_{as,\mathrm{BH_2,free}}$ (B_{1u}) absorbing at 1,174, 1,604, 2,519 and 2,608 cm^{-1}, respectively, many other bands are thought to be present for this system and in particular some controversial coupled overtones modes mentioned by Duncan et al. [26]. Even though several works have been devoted to the study of diborane, some properties, especially the vibrational properties, remain questionable [26–35]. Most of the investigations have been focused on the detection and assignment of all the fundamental vibrational frequencies, especially on the bending mode of the B–H bond in the cyclic diborane cluster. For instance, if we just take the controversial stretching mode, ν_{13}, the experimental values have varied a great deal over the time. Between 1950 and 1972, several data as 1999 [71], 1981 [26] to 1887 [71] cm^{-1} have been reported. In the 1980s, from the work of Duncan et al. [26, 31, 35], a reference up to now, the position of ν_{13} was settled at 1,924 cm^{-1}. This value is still mentioned in recent works as the experimental reference. However, one would realize that this value is not at all a pure experimental value, but rather, a theoretical estimation by using the parameters determined by the spectroscopy measurements (as mentioned in the introduction). Finally, the values from the calculations carried out by Duncan are nowadays cited in all references, but are overestimated, as shown by Lafferty et al. [30]. Indeed, these simulations are not accurate enough since couplings are limited to only two or three most closely lying vibrational states.

4.2 Assignments

We see now that it needs a new assignment for B_2H_6. Previous results seem to be too dependent to the mathematical model used by authors (see Table 2 and supplementary information). This is generally the sign of strong resonance. In reality, it is virtually impossible to have a universal tool that can both handle the increased flow of vibrational data (due to increased size of the chemical system studied, large amount of data from the force fields increased to nth order, etc.) and take into account all the vibrational interactions, which is the only guarantee of the quality of the result (apart from the quality of the PES). The choice of one or another approach to solving the RVSE depends on the specific information desired. To partially overcome this problem for the diborane medium-size molecules where all vibrational coupling are of prime importance, we have advanced our algorithm based on the vibrational distribution data for several independent spectral windows [48], that is, P_MWCI algorithm. In addition, at the price of generating the IC redundancy matrices, we have shown how the massive parallelization of the multiple windows CI approach [47], coupled to the generation of algorithms adapted to including the electrical anharmonicity [45] in the RVSE, allows us to achieve, by using a quasi-size-consistent approach, the finest effects (to the extent they are included in the PES).

As shown by data reported in Table 2 and in supplementary information, some characteristics remain uncertain, and the spectral data for many bands in a certain region data are found deviated from expected values. The main reason for these distortions is the presence of more than one resonance. The analysis of vibrational wavefunctions, the main results of which are shown in supplementary and in Table 2, shows that several modes are very strongly coupled, such that some overlaps exceed 33%. This phenomenon is unique for a system of this size. It is at the root of the difficulties during spectral interpretations offered over time by different authors in the literature as well as difficulties encountered by today's theorists while unquestionably assigning certain modes. If our variational results obtained with the double assumptions of mechanical and electrical anharmonicities appear broadly in good agreement with experimental values available, some constant contributions (for example, ν_9, in phase ω_{BH} in B_2H_6) prompted us to analyze in detail the impact of each coupling, whether it is introduced directly into the variational process or as the source of corrections to various perturbations. Also, calculations at the theoretical level lower than those offered at P_MWCI, that is, perturbation type (*P*), perturbation-variation (PV) and variation-perturbation (VP1 and VP4, developed in iterations of 1 and 4, respectively), were performed in addition to judge. For each vibrational state, (1) the direct impact of the absence of specific treatment of the resonances (*P*), (2) the impact of these that were introduced only around strong resonances and clearly identified initially during the reading of the PES (PV), and (3) the convergence of results when the indirect couplings are introduced progressively and iteratively in a variation-perturbation process. The results obtained for some of the most resonant modes are listed in Table 3. It is clear that from these examples, the overall consideration of all the resonances in the "brut force" variational process has a strong impact on the final accumulated results. The ν_2 and ν_{13} modes of B_2H_6 and the $\nu_5 + \nu_6$ et $\nu_5 + \nu_7$ overtones of B_2H_6 illustrate the importance of taking into account all the indirect couplings. Although the VP4 results for these modes are not completely inaccurate, they are nevertheless not precise enough to achieve a complete study of complex systems such as diborane. The perturbation and variation-perturbation treatments are, strictly speaking, more adapted to study large systems than precisely allocate the spectral data. The average difference between experiment and theory, as far as the experimentalists are aware, are on the order of 10.5 cm^{-1} calculated with P_MWCI and about 17, 28 and 52 cm^{-1} with VP4, PV, and perturbation, respectively. The overtone couplings involving two vibrational modes represent on average 77% of indirect couplings. The indirect couplings involving more than four different vibrational modes are neglected in our calculations, as their total contributions are less than 3%. The couplings resulted from those interactions of 4th order, impacting approximately 6%, on average, of the final result, may seem low. However, when a direct resonance is identified, these gaps widen sharply in favor of a "brut force" variational approach, and to a lesser extent, in favor of the iterative variational approaches.

Finally, based on the accurate variational data, we undertook to revisit and complete the experimental spectra of B_2H_6 and its deuterated derivative B_2D_6. If most fundamental bands could be clarified and assigned without ambiguity by combining our theoretical and experimental studies, this approach helped to highlight a number of overtones hitherto unreported in the previous works mainly because of their very low intensities. This is the case for the diborane molecule in the spectral region between 2,300 and 2,500 cm^{-1} where our calculations have allowed the search of few intense bands B_{3u} assigned to the overtones $2\nu_{10} + \nu_{17}$ and $\nu_7 + \nu_{10} + \nu_{15}$, respectively, observed at 2,323 and 2,327 cm^{-1}. Similarly, the overtone $\nu_3 + \nu_{10} + \nu_{12}$ calculated at 2,506 cm^{-1}, with a 2.56 km mol^{-1} intensity, was observed at 2,499 cm^{-1}. For the mode B_{2u} calculated at 2,478 cm^{-1} and assigned to the overtone $\nu_7 + \nu_{17}$, a few intense bands were observed at 2,469 cm^{-1} in our IR spectrum. In the same manner, the $\nu_3 + \nu_4 + \nu_{10}$ overtone belonging to the B_{1u} representation was observed at 2,394 cm^{-1}. In the spectral area between 2,500 and 2,900 cm^{-1}, our calculations predict at 2,594 cm^{-1} a relatively intense band assigned to the $\nu_5 + \nu_6$ mode, but this band was not observed experimentally. In return, the band observed at 2,877 cm^{-1}, not predicted theoretically, could be attributed to the $2\nu_9 + \nu_{14}$ overtone. More still, for

Table 2 Calculated and experimental (an)harmonic wavenumbers (in cm^{-1}) and intensities (km/mol) for $^{11}B_2H_6$

Mode description	Sym	Experimental		Theoretical			
			Our work	Ref.	Our work[a, h]		
		ω (cm^{-1})	ω (cm^{-1})	Frequencies (cm^{-1})	ω (cm^{-1})	ν (cm^{-1})	I (km mol^{-1})
ν_{18}, $\sigma_{BH_2,free}$ *opp phase*	B_{3u}	1,172[b] 1,159[i]	1,174	1,197[d] 1,174[e] 1,190[f] 1,175[k] 1,221, 1,190[n] 1,183[o] 1,220[p] 1,196.1[q]	1,197	1,187	70.57
$\nu_{10} + \nu_{12}$		1,283[b] 1,285[i]	1,282			1,319	2.49
ν_{17}, $\nu_{as,\ BH}$ *in phase*		1,603[b] 1,602.8[c] 1,585[i]	1,604	1,723[d] 1,690[e] 1,752[f] 1,615[k] 1,794, 1,599[n] 1,758[o] 1,772[p] 1,652.4[q]	1,717	1,567	352.02
$\nu_5 + \nu_{15}$		1,854[b] 1,845[i]	1,853			1,859*	0.25
$\nu_7 + \nu_{14}^{-}$						1,830—	17.7
$\nu_9 + \nu_{12}$		1,850[i]	1,849			1,912	0.23
$2\nu_{10} + \nu_{17}$			2,323			2,308***	1.18
$\nu_7 + \nu_{10} + \nu_{15}$			2,327			2,322***	0.12
$\nu_3 + \nu_{18}$		2,343[b]	2,344			2,387	13.57
$\nu_4 + \nu_{17}$		2,375[b] 2,364[i]	2,374			2,367	3.02
ν_{16}, $\nu_{s,\ BH}$ *opp phase*		2,520[b] 2,519[g] 2,510[i]	2,519	2,608[d] 2,613[e] 2,664[f] 2,518[k] 2,643, 2,537[n] 2,656[o] 2,639[p] 2,611.0[q]	2,618	2,535	76.64
$\nu_3 + \nu_{10} + \nu_{12}$			2,499			2,506^{+}	2.56
$\nu_7+\nu_{13}$							
$\nu_3 + \nu_{17}^{++}$		2,784[b] 2,755[i]	2,784, 2,790			?	
$\nu_{10} + \nu_{11}^{++}$		2,964[b] 2,962[i]	2,963			?	
$\nu_2 + \nu_{18}^{++}$		3,282[b] 3,257[i]	3,282			?	
ν_{15}, ω_{BH} *opp phase*	B_{3g}	1,006[i]	1,013	1,028[d] 1,029[e] 1,072[f] 1,023[k] 1,089, 1,091[n] 1,025[o] 1,071[p] 1,040.8[q]	1,030	1,007	0.01
ν_{14}, $\omega_{BH_2,free}$ *in phase*	B_{2u}	972[b] 972.9[c] 967[i]	973	990[d] 995[e] 1,016[f] 974[k] 1,017, 979[n] 1,008[o] 1,013[p] 992.8[q]	993	988	16.00
$\nu_{10} + \nu_{15}$		1,371[b] 1,377[i]	1,372			1,380	0.96
ν_{13}, $\nu_{s,\ BH}$ *in phase*		~1,879[b] 1,880[i]	1,880	2,000[d] 1,988[e] 2,036[f] 1,924[k] 2,033, 1,930[n] 2,017[o] 2,051[p] 1,984.3[q]	2,009	1,871**	7.43
$\nu_9 + \nu_{15}$		1,990[b] 1,991[i] 1,992[j]	1,990			2,023	2.20
$\nu_4 + \nu_{14}^{-}$							
$\nu_4 + \nu_{13}$							
$\nu_7 + \nu_{17}$			2,469			2,478	0.78
$\nu_{12} + \nu_{17}$							
ν_{12}, $\delta_{as,BH_2,free}$	B_{2g}	?915[b]		940[d] 930[e] 942[f] 918[k] 961, 942[n] 929[o] 961[p] 933.7[q]	941	936	0.00
ν_{11}, $\nu_{as,BH_2,free}$ *opp phase*				2,695[d] 2,718[e] 2,791[f] 2,597[k] 2,739, 2,616[n] 2,772[o] 2,733[p] 2,690.3[q]	2,706	2,605	0.00
ν_{10}, τ	B_{1u}	368.8[m] 379[i]	?	395[d] 377[e] 329[f] 367[k] 393, 376[n] 376[o] 378[p] 376.1[q]	361	361	11.49
ν_9, ω_{BH} *in phase*		?950[b] 937.4[c] 934[i]	986	950[d] 920[e] 933[f] 951[k] 1,006, 963[n] 949[o] 982[p] 968.4[q]	960	945	1.00
$\nu_4 + \nu_{10}$		1,187[c]	1,187			1,150	0.01
$\nu_3 + \nu_{10}$		1,552.5[c]	1,569			1,542	0.02
$\nu_5 + \nu_7$							
$\nu_3 + \nu 9$			1,585			1,586	1.08
$\nu_{10} + 2\nu_4$			–			1,960	0.20
$\nu_{14} + \nu_{15}^{-}$		1,970[i]	1,993			2,016	0.48
$\nu_{12} + \nu_{18}$			2,060 ?				
$\nu_3 + \nu_4 + \nu_{10}$			2,394			2,401	0.21
ν_8, $\nu_{as,BH_2,free}$ *in phase*		2,609[b] 2,610[g] 2,597[i]	2,608	2,710[d] 2,735[e] 2,808[f] 2,613[k] 2,751, 2,630[n] 2,785[o] 2,745[p] 2,703.5[q]	2,721	2,610	0.48
$\nu_5 + \nu_6$			Undefined			2,594	6.63
$\nu_1 + \nu_{10}^{++}$?		~2,870[b] 2,869[i]				?	
$2\nu_9 + \nu_{14}^{++}$?		2,873[b]	2,877			?	
$\nu_{13} + \nu_{15}$							
$\nu_1 + \nu_9^{///}$							

Table 2 continued

Mode description	Sym	Experimental		Theoretical			
			Our work	Ref.	Our work[a, h]		
		ω (cm^{-1})	ω (cm^{-1})	Frequencies (cm^{-1})	ω (cm^{-1})	ν (cm^{-1})	I (km mol^{-1})
ν_7, $\omega_{BH_2,free}$ *opp phase*	B_{1g}			894[d] 878[e] 896[f] 860[k] 920, 882[n] 894[o] 929[p] 877.6[q]	889	871	0.00
$\nu_5 + \nu_{10}$		~1,170–1,180[c]				1,183	0.00
ν_6, $\nu_{as,\ BH}$ *opp phase*				1,861[d] 1,842[e] 1,924[f] 1,756[k] 1,929, 1,762[n] 1,883[o] 1,942[p] 1,814.4[q]	1,856	1,750	0.00
ν_5, $\tau_{BH_2,free}$ *opp phase*	A_u	833[b] 830[l]	831	850[d] 878[e] 896[f] 833[k] 868, 864[n] 831[o]874[p] 850.1[q]	847	838	0.00
$\nu_4 + \nu_5$		1,616.5[c]	1,610			1,612	0.00
ν_4, ν_{B-B}	A_g			799[d] 788[e] 809[f] 788[k] 820, 795[n] 816[o] 824[p] 798.0[q]	802	789[++++]	0.00
ν_3, $\sigma_{BH_2,free}$ *in phase*				1,207[d] 1,181[e] 1,196[f] 1,187[k] 1,235, 1,204[n] 1,198[o] 1,229[p] 1,207.1[q]	1,205	1,195	0.00
$\nu_9 + \nu_{10}$[++]		?1,318[b]	1,314		1,309	1,308	0.00
ν_2, $\nu_{s,\ BH}$ *in phase*		?2,112[b]		2,185[d] 2,164[e] 2,206[f] 2,096[k] 2,221, 2,101[n] 2,203[o] 2,217[p] 2,152.6[q]	2,197	2,117[+++]	0.00
ν_1, $\nu_{s,BH_2,free}$ *in phase*				2,621[d] 2,629[e] 2,686[f] 2,526[k] 2,659, 2,550[n] 2,676[o] 2,653[p] 2,622.0[q]	2,633	2,534	0.00

1,170 cm^{-1} corresponds to the hot $\nu_{10} + \nu_{18} - \nu_{10}$ band ($^{11}B_2H_6$)

? Uncertain assignment

[*] Strong resonance with $\nu_{14} + \nu_7$ (32%) located at 1,828 cm^{-1} B_{3u}

[**] Strong resonance with $\nu_9 + \nu_{15}$ (22%) located at 2,023 cm^{-1} B_{2u}

[***] Strong resonance between $2\nu_{10} + \nu_{17}$ and $\nu_{10} + \nu_7 + \nu_{15}$ (16%)

[+] Strong resonance with ν_{16} (18%) located at 2,520–2,535 cm^{-1} B_{3u}

[++] Ducan attribution

[+++] Not pure, that is, 70% for ν_2 and 81% for ν_1 in $^{11}B_2D_6$, and 45% for ν_1 in $^{11}B_2H_6$ (see Ref. [25])

[++++] Resonance with $2\nu_{10}$ (16%) located at 750 cm^{-1} A_g. This coupling is not present for the $^{11}B_2D_6$ compound (in disagreement with the Ref. [26])

[-] Strong resonance with ν_{13} (36%) located at 1,484 cm^{-1} B_{2u}

[–] Undefined contour for Ref.[b] assigned to $\nu_9 + \nu_{12}$

[—] Strong resonance with $\nu_9 + \nu_{12}$ (20%) located at 1,450 cm^{-1} B_{3u}

[——] Very strong resonance with both $\nu_5 + \nu_{15}$ (33%) located at 1,859 cm^{-1} B_{3u} and $\nu_{12} + \nu_9$ (11%) located at 1,849 cm^{-1} B_{3u}

[/] Strong resonance with ν_{16} (25%) located at 1,860 cm^{-1} B_{3u}

[//] Resonance with $2\nu_5 + \nu_9$ (12%) located at 1,863 cm^{-1} B_{3u}

[///] Resonance with both $\nu_9 + 2\nu_{15}$ (16%) located at 2,099 cm^{-1} and $\nu_{13} + \nu_{15}$ (12%) located at 2,098 cm^{-1} B_{1u}

[a] This work: B3LYP/6-31+G** *harmonic values,* anharmonic values (activities)

[b] Gas phase [26]

[c] High-resolution infrared study [27]

[d] Harmonic values B3LYP/TZ2P [28]

[e] Harmonic values B3LYP/DZP [29]

[f] Harmonic values MP2/DZP [29]

[g] Experimental [30]

[h] Coriolis effect superior to 3 cm^{-1} is only reported. 3 cm^{-1} on the mode number 1 will be noted 1(3). 1(3), 2(3), 5(5), 7(5), 8(3), 9(3), 10(5), 11(4), 13(6), 14(4), 15(4) and 16(4) for $^{11}B_2H_6$. 5(3), 7(3), 8(3), 10(3), 13(3), 15(3) and 16(3) for $^{11}B_2D_6$

[i] Crystalline films of $^{11}B_2H_6$ [26]

[j] Gas phase [72]

[k] Anharmonic prediction realized on the basis of experimental and harmonic data [31]

[l] [72]

[m] High-resolution infrared study [73]

[n] Anharmonic treatment—Perturbational approach. CCSD/TZ2P [32]

[o] Harmonic CCSD/DZP [33]

[p] Harmonic MP2/TZ2P + *f* [34]

[q] Experimental harmonic frequencies [35]

Table 3 Some examples of mathematical treatments of vibrational resonant states couplings

	Perturbation	Perturbation-variation	Variation-perturbation		Variation	Experimental[a]
			$\gamma = 1$	$\gamma = 4$		
$^{11}B_2H_6$						
ν_{15}, ω^{BH} *opp phase*	1,030	1,024	1,029	1,009	1,007	1,013
ν_{13}, $\nu_{s,\ BH}$ *in phase*	2,009	1,930	1,951	1,900	1,871	1,880
ν_2, $\nu_{s,\ BH}$ *in phase*	2,197	2,130	2,129	2,140	2,117	2,112
$^{11}B_2D_6$						
$\nu_9 + \nu_{12}$	1,433	1,441	1,472	1,453	1,450	1,453
$\nu_3 + \nu_{10}$	1,151	1,163	1,192	1,190	1,183	1,189
$\nu_5 + \nu_7$	1,288	1,331	1,391	1,338	1,325	~1,270 ?
$\nu_5 + \nu_6$	1,837	1,844	1,870	1,866	1,852	1,857
$\nu_9 + \nu_{10}$	986	980	980	975	957	?966

? Uncertain assignment

[a] See ref. listed in Table 2 and in supplementary information

symmetry B_{1u}, the vibration $\nu_9 + \nu_3$ not observed in previous works is proposed at 1,585 cm^{-1}. For the deuterated compound, the compared results issued from our calculations and the new spectral observed analysis show that the $\nu_9 + \nu_{12}$ and $\nu_{13} + \nu_7$ overtone bands are, respectively, assigned to the peaks centered at 1,453 and 2,146 cm^{-1}. The band observed at 1,729 cm^{-1} is assigned to the polyad $\nu_7 + \nu_{10} + \nu_{15}$ based on our calculations. Our computational results provide also that the mode calculated at 1,860 cm^{-1} with an intensity of 2.66 km mol^{-1} assignable to $\nu_4 + \nu_{17}$ overtone might correspond to the experimentally observed band centered at 1,877 cm^{-1}.

5 Conclusion

A pure variational approach, developed in both mechanical and electrical anharmonicities, was applied to study the diborane molecule for which many uncertainties persist in the spectral IR assignment. This molecule has been the subject of many experimental and theoretical studies, often in contradiction with each other, especially regarding the description of the fundamental modes ν_2, ν_{15} and the very controversial ν_{13}. The pure variational P_MWCI method was applied to introduce both direct and indirect vibrational couplings. The weight of indirect coupling was for the first time estimated. The analysis of vibrational wavefunctions of some resonant states shows that several modes are very strongly coupled, such that some overlaps exceed 33%. Unfortunately, if taking into account only the main interactions in this vibrational process with the size sufficiently reduced by reducing the vibrational couplings in the mathematical process, it would not be able to explicitly address all the vibrational interactions, and therefore, would be insufficient to predict accurately and systematically some of the most critical resonances. Nevertheless, we have to temper our previous conclusion. Indeed, we cannot claim neither that fully variational methods can automatically lead to the most accurate predictions (see, in particular, setbacks obtained in the electronic computations for excited states descriptions) nor that it is impossible to accurately manage the variational space by mixed variational-perturbation approaches. So, fully variational methods are not universal, but are very efficient in some critical case descriptions like indirect resonance phenomena.

Finally, this work, together with all the experiments on this system during the past decades, shows the difficulty of interpreting the spectral data, making it a "benchmark" ideal for testing the mathematical approaches for implementation of mathematical methods.

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