

Ab initio Vibration-Rotation Spectroscopy

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Abstract: This review surveys recent theoretical work from our group in the area of vibration-rotation spectroscopy. It addresses the computation of anharmonic force fields and spectroscopic constants in the context of rovibrational perturbation theory as well as variational calculations of vibrational levels, on the basis of highly accurate *ab initio* potential energy surfaces. Results are presented for three case studies involving difluorovinylidene, bismuthine, and ammonia, to illustrate current contributions from *ab initio* quantum chemistry to spectroscopic studies.

Keywords: Ammonia · Computational chemistry · Force fields · Reactive molecules · Spectroscopy

1. Introduction

High-level *ab initio* quantum chemistry is a natural partner of high-resolution spectroscopy. On the one hand, the quality of *ab initio* calculations can be gauged by comparison with accurate spectroscopic data. On the other hand, after such validation, *ab initio* theory can provide realistic predictions which may guide the spectroscopic identification of unknown reactive molecules and assist in the analysis and assignment of high-resolution spectra.

This article reviews some of our recent theoretical work on vibration-rotation spectroscopy which addresses both of these objectives. The prediction of theoretical vibration-rotation spectra requires knowledge of the potential energy and dipole moment surfaces which can be computed using electronic structure theory. These quantum-chemical data can then be converted into spectroscopic information using either rovibrational perturbation theory or variational treatments of nuclear motion. These two approaches will be discussed in sections 2 and 3, respectively, followed by a brief summary in section 4.

2. Anharmonic Force Fields and Spectroscopic Parameters

The harmonic-oscillator rigid-rotor approximation provides the simplest textbook model for vibration-rotation spectroscopy: each vibration is independent and represented by a normal mode, and the molecule rotates as a rigid body. Second-order perturbation theory can then be employed to account for the anharmonic coupling between the vibrations and the vibration-rotation coupling due to nonrigid rotation. This treatment yields an effective Hamiltonian and expressions for the rovibrational levels in terms of quantum numbers and spectroscopic constants. The experimental high-resolution spectra are interpreted on the basis of such effective Hamiltonians, and the spectroscopic constants are determined through appropriate fits of the observed spectral lines.

In the context of second-order perturbation theory [1][2], there are explicit formulas that relate the spectroscopic constants of a given molecule to its equilibrium geometry and its quartic force field (*i.e.* the derivatives of the potential energy with respect to the nuclear coordinates, evaluated at the equilibrium geometry up to fourth order). *Ab initio* methods can be applied to compute these molecular properties. Due to the availability of analytic second derivatives for most of the established methods, it is nowadays routine to calculate the equilibrium geometry and the quadratic force field. The required cubic and quartic force constants are best determined from analytic second derivatives by a numerical finite-difference procedure [3] that involves displacements along normal coordinates and yields all cubic and semi-

diagonal quartic force constants which are needed in the equations for the spectroscopic constants [1–3]. In this procedure, the numerical precision of the results must be controlled carefully, through an appropriate choice of step sizes and tight convergence criteria for the quantum-chemical calculations and for geometry optimization. Suitable guidelines are available for this purpose [3][4].

As illustrated in Fig. 1, the spectroscopic constants provide the meeting ground between theory and experiment in the standard approach outlined above. The next question is obvious: How accurate are current *ab initio* calculations for these spectroscopic parameters? This can be tested in systematic convergence studies using increasingly accurate levels of theory and basis sets. Fig. 2 and 3 show corresponding results for the geometry and the harmonic vibrational wavenumbers of water, respectively. Three levels of theory have been applied (SCF: self-consistent-field Hartree-Fock theory, MP2: second-order Møller-Plesset perturbation theory; CCSD(T): coupled cluster theory with single and double excitations augmented by a perturbational treatment of connected triple excitations), in combination with five correlation-consistent polarized valence basis sets of increasing size (from cc-pVDZ to cc-pV6Z, with 24 to 322 basis functions). The results are seen to converge at each level as the size of the basis approaches the complete basis set (CBS) limit. The converged Hartree-Fock results deviate considerably from the experimental data, which are however well reproduced upon inclusion of electron correlation at the simple MP2 level and particularly at the more accu-

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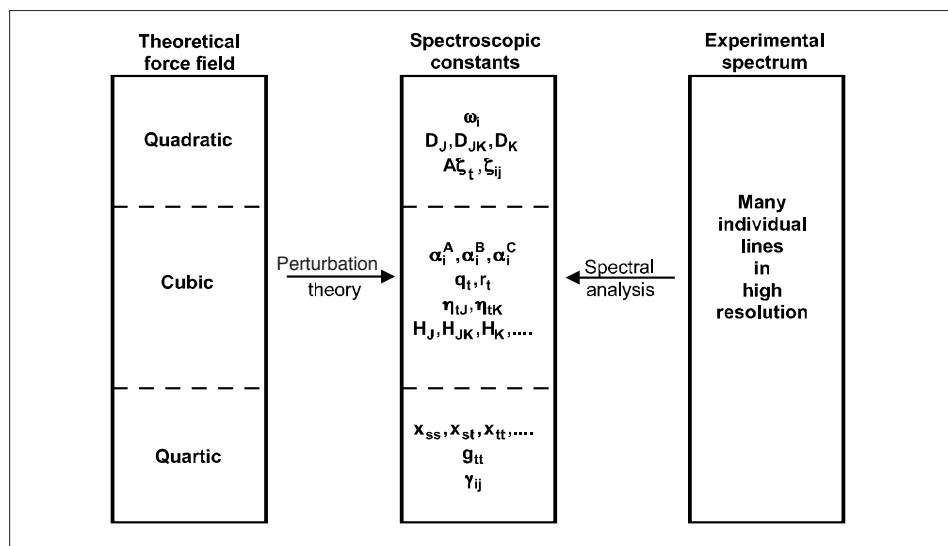
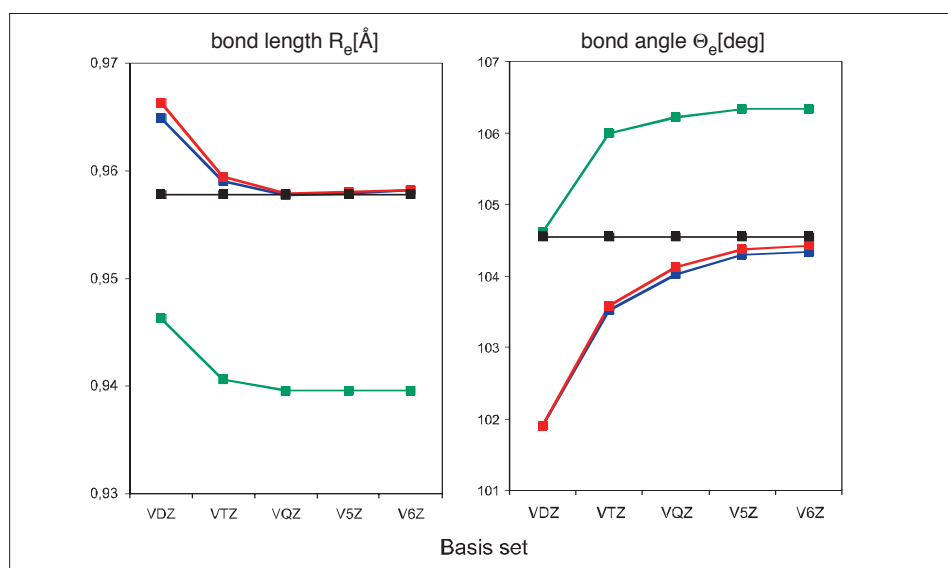
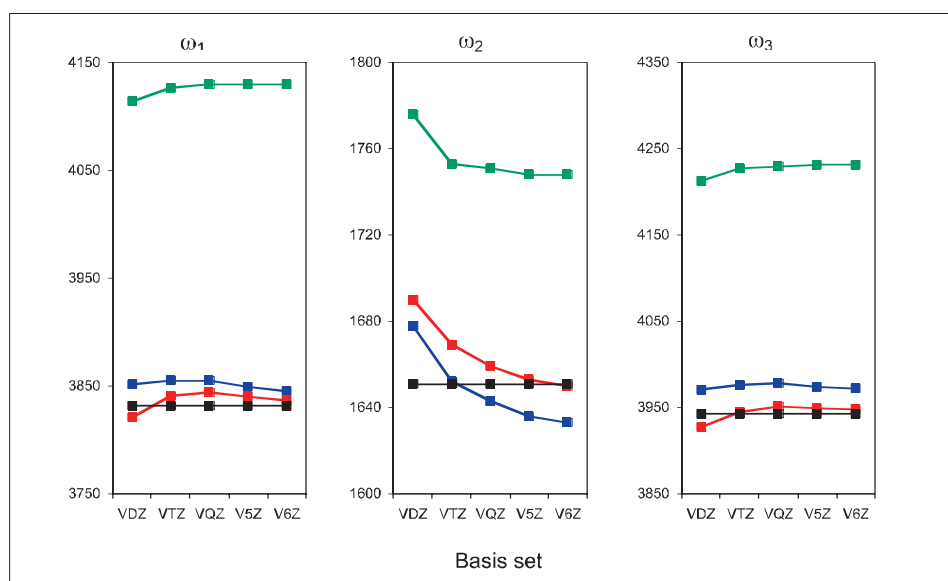


Fig. 1. Spectroscopic constants: theory meets experiment

Fig. 2. Equilibrium geometry of water: convergence of *ab initio* results. Color code: green SCF, blue MP2, red CCSD(T), black experiment. The cc-pVnZ basis sets are denoted as VnZ (n=D,T,Q,5,6).Fig. 3. Harmonic wavenumbers of water: convergence of *ab initio* results. See caption of Fig. 2 for notation.

rate CCSD(T) level. The superiority of CCSD(T) over MP2 becomes more obvious for electronically more demanding molecules such as HOF and F_2O [4]. Based on many such convergence studies, we find that CCSD(T) calculations with the cc-pVQZ basis are usually adequate for molecular geometries and harmonic force fields: bond lengths are normally given within 0.2 pm, bond angles within 0.2° , and harmonic wavenumbers within 10 cm^{-1} (or typically 1%). Concerning the quartic force fields, MP2/cc-pVTZ yields reasonable estimates of anharmonic spectroscopic constants such as the vibration-rotation interaction constants α_i^X and the anharmonicity constants x_{ij} (often within 20%), whereas CCSD(T)/cc-pVTZ is recommended for higher accuracy (often within 5%). Larger basis sets such as cc-pVQZ are normally not needed for anharmonic force fields.

Having established an efficient and reliable computational approach, it is possible to predict the vibration-rotation spectra and other properties of yet unknown molecules in order to assist in their spectroscopic identification. This will now be illustrated for the example of difluorovinylidene $F_2C=C$. Vinylidenes are elusive reactive intermediates. The parent compound (singlet $H_2C=C$) and 1-H-vinylidenes rearrange easily into alkynes, by a very facile 1,2-H-shift with a barrier of *ca.* 1–4 kcal/mol. $F_2C=C$ is a more promising target because the barrier to a 1,2-F-shift is much higher. Consequently, there have been several attempts to detect $F_2C=C$, and a vibrational progression in the photoelectron spectrum of the corresponding anion has indeed been attributed to $F_2C=C$ [5]. Our CCSD(T) calculations show that $F_2C=C$ has to overcome a barrier of 36 kcal/mol to rearrange to difluoroethyne FCCF which is more stable than $F_2C=C$ by 29 kcal/mol. It is therefore most unlikely that $F_2C=C$ can be prepared from FCCF by a thermal reaction, but when generated photochemically from FCCF it should live long enough to be detectable. Irradiation of matrix-isolated FCCF in Ar at 10 K with a pulsed 193 nm ArF laser yields a photolysis product [6] that exhibits several sharp infrared lines (Fig. 4). Through comparison with the computed *ab initio* gas-phase spectrum (red in Fig. 4) these lines can unambiguously be assigned to $F_2C=C$. Their positions are predicted by the *ab initio* calculations within the expected accuracy of about 10 cm^{-1} , both for the six fundamental bands ν_1 and for the combination band $\nu_2+\nu_5$ which is in anharmonic resonance with ν_4 . Moreover, their intensities are also predicted well from the calculated dipole moment derivatives (double harmonic approximation) including those for the very weak bending modes ν_3 and ν_6 . Hence, there is no doubt that $F_2C=C$ can indeed be made photochemically in an Ar matrix [6]. $F_2C=C$ behaves as a superelectrophilic carbene and reacts with

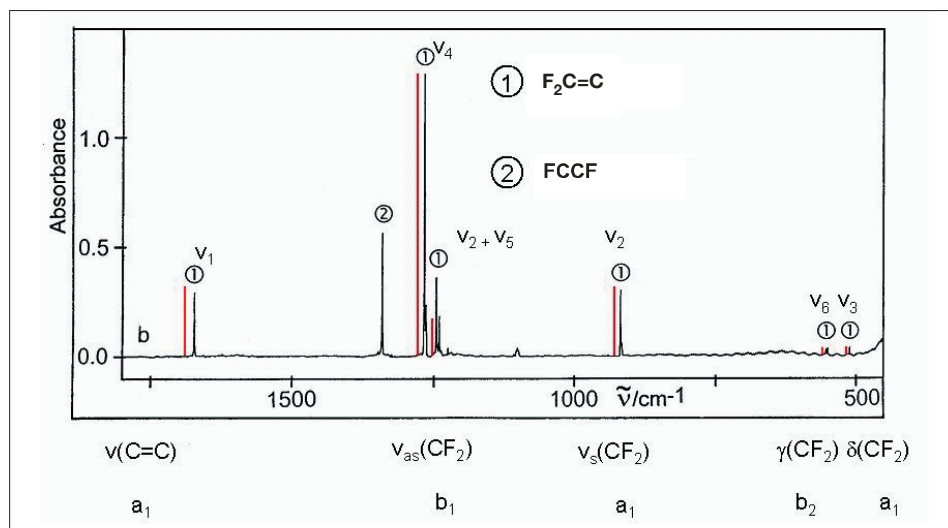


Fig. 4. Matrix infrared spectrum (black) of a photostationary mixture of difluorovinylidene and difluoroethyne in Ar at 10 K, and computed gas-phase infrared spectrum of difluorovinylidene (red)

many nucleophiles added to the Ar matrix [7]. Even with xenon, it forms a charge-transfer complex $F_2C=CXe$ which has again been identified and characterized with the aid of *ab initio* calculations [8]. Experimentally, it has unfortunately not been possible, in spite of many attempts, to measure gas-phase high-resolution spectra of photochemically generated $F_2C=C$. The *ab initio* results for the equilibrium geometry and various harmonic and anharmonic spectroscopic constants of $F_2C=C$ thus serve as predictions [9] that may hopefully be verified in future experimental work.

Using the combined theoretical and experimental approach outlined above, we have characterized a number of reactive and short-lived molecules over the past years, mostly in close cooperation with the group of Hans Bürger [10]. This includes joint work on difluorophosphorane PH_2F_2 [11], difluoroethyne $FCCF$ [10][12–14], fluorochloroethyne $FCCl$ [10][15], silaethene $H_2C=SiH_2$ [16–18], difluorosilanethione $F_2Si=S$ [19], phosphinous fluoride $FP=O$ [20], thiophosphinous fluoride $FP=S$ [21][22], the fluorocarboxyl radical FCO_2 [23], and bismuthine BiH_3 [24–26]. Here we briefly comment only on the most recent study of bismuthine, the heaviest and least stable XH_3 species of group 15 ($X=N,P,As,Sb,Bi$). Experimentally, the challenging synthesis [27] of BiH_3 could be repeated successfully such that it became possible to record high-resolution vibrational and rotational spectra [24][25]. From a theoretical point of view, the presence of a heavy atom (Bi) poses two problems that are not encountered with lighter atoms and may limit the accuracy of our calculations: it is practically inevitable to replace the inner-shell core electrons by a suitable pseudopotential, and it may be necessary to explicitly account for valence-shell relativistic effects. A systematic investigation of these and other is-

ues [24–26] has led to the conclusion that outer-core correlation in the $5s5p5d$ shell is important in BiH_3 and strongly affects the bond length (by almost 2 pm) and the stretching wavenumbers (by about 20 cm^{-1}). Therefore it is necessary to employ small-core pseudopotentials and explicitly correlate the outer-core electrons. This treatment requires very large basis sets at Bi to avoid basis set superposition errors, and the recommended optimized [8s8p7d5f3g2h] basis at Bi contains 151 basis functions (aug-cc-pVQZ at H). CCSD(T) calculations with this extended basis and a relativistic pseudopotential yield satisfactory results for the equilibrium geometry and the fundamental wavenumbers for the bending modes, while those for the stretching modes are overestimated more strongly than usually found at this level of theory. This is rectified by including relativistic spin-orbit corrections from an appropriate spin-orbit configuration interaction (CI) treatment which lowers the stretching wavenumbers by up to 12 cm^{-1} . After these measures, the *ab initio* results for BiH_3 reproduce the experimental data well [24–26] and satisfy our target accuracy (see above). Hence, the available *ab initio* methods can describe heavy closed-shell molecules with similar accuracy as compounds consisting only of lighter elements.

A final point in this section concerns analogous applications of density functional theory (DFT). The procedures for computing anharmonic force fields can also be employed at the DFT level, provided that numerical issues are handled with proper care [28]. DFT results for spectroscopic constants are normally of similar accuracy to MP2 results, except for occasional outliers [28], and DFT has the advantage that it can often still be used in electronically demanding situations, e.g. for transition metal compounds, where single-reference *ab initio* methods such as MP2 or CCSD(T) may fail. One such

example is permanganyl fluoride MnO_3F [29]. Another obvious advantage of DFT is its rather low computational cost compared with high-level *ab initio* methods, and it can therefore be used to calculate anharmonic force fields for medium-sized molecules such as benzene [30] and azabenzene [31]. While the validation studies on DFT anharmonic force fields [28][32][33] generally show reasonable performance of the established functionals, the DFT results cannot be improved systematically (unlike *ab initio* results) which is a major disadvantage. Whenever feasible in practice, it is therefore advisable to employ high-level *ab initio* methods in connection with high-resolution spectroscopic studies on small molecules. DFT will be the method of choice for larger molecules, and especially for transition metal compounds, when the emphasis is on qualitatively reliable results: these can often already be obtained from harmonic DFT force fields [34][35].

3. Potential Energy Surfaces and Vibrational Levels

The standard approach outlined in the preceding section is usually appropriate for describing the fundamental vibrations of semirigid molecules. It is less suitable for vibrationally excited polyatomic molecules with high vibrational energy and for floppy molecules with large amplitude motions. In such cases, it is necessary to resort to a variational treatment of molecular motion [36]. The variational approach requires an accurate potential energy surface (PES) for the configurational space that is sampled during the vibrations, along with a corresponding dipole moment surface (DMS) if intensities are of interest. These *ab initio* surfaces are computed at a large number of grid points and then represented by a suitable analytic function through least-squares fitting. The actual variational treatment proceeds as follows: After choosing appropriate basis functions (e.g. Morse oscillators for stretching and harmonic oscillators for bending) and setting up the Hamiltonian (explicit kinetic energy expressions plus the analytic potential function), the Hamiltonian matrix is calculated and diagonalized to obtain the vibrational levels and eigenfunctions. The exact solution for a given input potential can be reached by converging the variational results with regard to the chosen basis set for nuclear motion. For this reason, the variational approach is superior to second-order perturbation theory (section 2) with regard to the accuracy that can be achieved, but it is also considerably more costly.

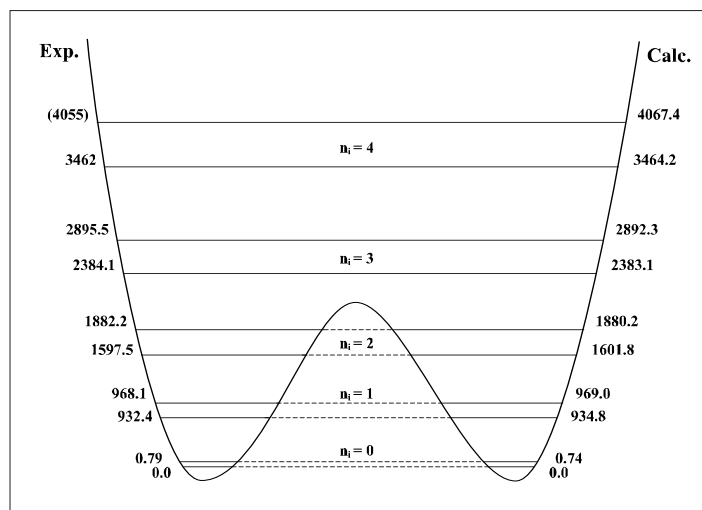
A recent benchmark study on water [37] illustrates the state of the art in exact variational calculations on triatomic molecules. The underlying PES has been determined by

multi-reference MRCI calculations with very large basis sets (up to aug-cc-pV6Z) and extrapolation to the CBS limit, augmented by corrections for core-valence correlation, relativistic effects, quantum electrodynamics, and diagonal Born-Oppenheimer terms. The quality of the computed vibrational levels has been evaluated through comparisons with the 104 experimentally known vibrational band origins up to about 25000 cm^{-1} . The corresponding root-mean-square (rms) deviations decrease systematically with improvements in the PES, typical values [37] being 16.56 cm^{-1} for MRCI/CBS, 4.23 cm^{-1} for MRCI/CBS plus core-valence correlation and relativistic corrections, and 1.90 cm^{-1} after including all corrections considered. This accuracy is truly remarkable, especially when taking into account that the standard deviations are much smaller in the low-energy region, by more than a factor of 2. Individual positions of rovibrational lines (*i.e.* differences between rovibrational levels connected by an allowed transition) are typically accurate to 0.2 cm^{-1} due to the cancellation of systematic errors [37].

Our own variational calculations have focused on ammonia which exhibits a low inversion barrier of less than 1800 cm^{-1} and is therefore the prototype of a molecule with large amplitude inversion motion. It is obvious that a variational approach is needed for a proper understanding of the vibration-rotation-inversion spectrum of ammonia. Theoretical challenges associated with this endeavor include the computation of accurate six-dimensional (6D) PES and DMS, the best choice for the 6D variational treatment of nuclear motion, the description of rotationally excited states, the evaluation of line intensities, and the simulation of tunneling dynamics. Given these many challenges, it is not surprising that several groups have recently been attracted to ammonia and are currently studying these topics [38–51]. For the sake of brevity, we shall only survey our own investigations in this area [50][51].

In our published work on ammonia [50] we have generated 6D PES and DMS at the CCSD(T)/aug-cc-pVTZ level using a regular grid of 14400 points. For a subset of 1244 points, more accurate energies (labelled CBS+) have been computed by extrapolating the CCSD(T) energies to the CBS limit and adding core-valence correlation and relativistic corrections; another 389 CBS+ data are available on a denser two-dimensional (2D) grid for C_{3v} symmetric geometries. The differences between CCSD(T)/aug-cc-pVTZ and CBS+ energies form a rather smooth surface (EDS) which can be represented by an interpolated or fitted function to provide corrections for all those points where only CCSD(T)/aug-cc-pVTZ data are available. Adding these corrections from EDS interpolation or fitting yields CBS* or

Fig. 5. Inversion potential and inversion levels (cm^{-1}) in ammonia. The experimental value of 4055 cm^{-1} is uncertain (stated error bar of 5 cm^{-1}). The other experimental levels and inversion splittings are well reproduced by the calculations.



CBS** PES, respectively, which are of similar quality to the target CBS+ PES. Our vibrational energy calculations are based on the Hougen-Bunker-Johns (HBJ) formalism [52] involving a nonrigid reference configuration that follows the large amplitude inversion motion of ammonia. The latter is described by a trigonometrically defined inversion coordinate (corresponding to the angle between the C_3 axis and an N–H bond in the C_{3v} case), while the five small amplitude vibrations are treated as displacements from this nonrigid reference configuration and expressed in terms of Morse coordinates for the three N–H stretches and internal symmetry coordinates for the remaining two bends. The analytic representations of the *ab initio* PES employ fourth-order polynomials of these coordinates, with up to 78 prefactors that are determined by least-squares fits. In the HBJ formalism, the Hamiltonian contains an approximate kinetic energy operator that is derived by a Sorensen procedure [53] with Eckart-Sayvets constraints and involves expansions in linearized internal coordinates. For consistency, the analytic potential function is also reexpanded in terms of these linearized coordinates up to fourth order. The Hamiltonian matrix is then constructed in a basis set whose functions are products of Morse oscillator functions for stretching, two-dimensional isotropic harmonic oscillator functions for bending, and numerical inversion functions obtained by numerically solving the one-dimensional inversion problem. Diagonalization of the Hamiltonian matrix finally yields the vibrational energy levels.

Concerning our published results on ammonia [50], the CBS+ inversion barrier is 1790 cm^{-1} which is lowered to 1766 cm^{-1} by including an improved core-valence correlation and a diagonal Born-Oppenheimer correction. These values are close to the best available theoretical estimate of $1777 \pm 13\text{ cm}^{-1}$ [54]. The computed vibrational energy levels can be compared to experimentally observed vibrational band centers with un-

ambiguous assignments: 56 bands in NH_3 up to 15500 cm^{-1} have been chosen for this purpose as well as 50 bands in its isotopomers up to 5100 cm^{-1} . The rms deviation between experiment and theory for all bands in NH_3 is 34 cm^{-1} for the CCSD(T)/aug-cc-pVTZ surface, and ranges from $13\text{--}16\text{ cm}^{-1}$ for the more accurate surfaces such as CBS+ and CBS* [50]. Lower-energy levels are reproduced more accurately, *e.g.* for the 28 fundamental bands of all isotopomers considered (rms deviations less than 5 cm^{-1} for CBS+-type surfaces). Inversion splittings are computed even more accurately, typically within 2 cm^{-1} of experiment, which is illustrated in Fig. 5 for the umbrella mode ν_2 and its overtones.

While these results for ammonia are quite encouraging, they are certainly less accurate than the benchmark results for water [37] (see above). We have therefore tried to improve them by further refining our theoretical approach [51]. The regular grid has been extended from 14400 to 45760 points, and another 6056 points with energies up to about 20000 cm^{-1} have been added outside this grid to cover all low-energy regions in 6D space. CCSD(T)/aug-cc-pVTZ and CBS** energies are available at all these points. The analytic PES representations have been upgraded from fourth-order to sixth-order polynomials, which reduces the rms error of the PES fits typically from $4\text{--}6\text{ cm}^{-1}$ to $2\text{--}3\text{ cm}^{-1}$. The reexpansions of the kinetic and potential energy terms in the Hamiltonian have been extended to eighth order and sixth order, respectively, and convergence to better than 0.1 cm^{-1} has been demonstrated for the approximate kinetic energy operator. Each of these improvements in our computational approach leads to some improvement in the computed vibrational energies. Their combined effect is a general shift upwards, by about 10 cm^{-1} , and a reduction of the rms deviations between experiment and theory to the range of $5\text{--}10\text{ cm}^{-1}$, for CBS** and related surfaces. These new results [51] are more satisfactory

than the published ones [50], but they are still less accurate than the corresponding benchmark results for water [37] with rms deviations of about 4 cm^{-1} at a comparable theoretical level (see above). It should be kept in mind, however, that ammonia is more difficult to treat than water, because of the large amplitude inversion motion and the higher dimensionality (6D vs. 3D). In view of these complications, we feel that the accuracy of our variational results on ammonia is acceptable and that our best *ab initio* 6D PES describe the vibrational energies indeed quite well up to relatively high energies. An extension of this work to excited rovibrational states and to intensities is in progress.

4. Conclusions

The standard perturbational approach (section 2) and the variational approach (section 3) to *ab initio* vibration-rotation spectroscopy are complementary to each other. The former works well for calculating the spectroscopic parameters of semirigid molecules, whereas the latter is the method of choice for floppy molecules with large amplitude motions, and generally when highly accurate results are required, particularly in the high-energy region. Both approaches rely on accurate potential energy surfaces from quantum chemistry: coupled cluster treatments such as CCSD(T) have become the standard choice in this regard for molecules which can be described by single-reference methods.

The case studies presented highlight different aspects. The joint work on $\text{F}_2\text{C}=\text{C}$ and BiH_3 demonstrates the advantages of a combined experimental and theoretical approach to the spectroscopy of reactive short-lived molecules. The variational calculations on ammonia push the limits of the accuracy that can be reached in a demanding application. Taken together, these case studies are intended to illustrate the possible contributions from current *ab initio* quantum chemistry in this field.

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