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QUANTUM CHEMICAL B3LYP/cc-pvqz COMPUTATION OF GROUND-STATE STRUCTURES AND PROPERTIES OF SMALL MOLECULES WITH ATOMS OF Z ≤ 18 (HYDROGEN TO ARGON)

(IUPAC Technical Report)

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Quantum chemical B3LYP/cc-pvqz computation of ground-state structures and properties of small molecules with atoms of $Z \leq 18$ (hydrogen to argon)

(IUPAC Technical Report)

Abstract: Since density functional theory (DFT) achieved a remarkable breakthrough in computational chemistry, the important general question "How reliable are quantum chemical calculations for spectroscopic properties?" should be answered anew. In this project, the most successful density functionals, namely the Becke B3LYP functionals, and the correlation-consistent polarized valence quadruple zeta basis sets (cc-pvqz) are applied to small molecules. In particular, the complete set of experimentally known diatomic molecules formed by the atoms H to Ar (these are 214 species) is uniformly calculated, and calculated spectroscopic properties are compared with experimental ones. Computationally demanding molecules, such as open-shell systems, anions, or noble gas compounds, are included in this study. Investigated spectroscopic properties are spectroscopic ground state, equilibrium internuclear distance, harmonic vibrational wavenumber, anharmonicity, vibrational absolute absorption intensity, electric dipole moment, ionization potential, and dissociation energy. The same computational method has also been applied to the ground-state geometries of 56 polyatomic molecules up to the size of benzene. Special sections are dedicated to nuclear magnetic resonance (NMR) chemical shifts and isotropic hyperfine coupling constants. Each set of systems for a chosen property is statistically analyzed, and the above important question "How reliable...?" is mathematically answered by the mean absolute deviation between calculated and experimental data, as well as by the worst agreement. In addition to presentation of numerous quantum chemically calculated spectroscopic properties, a corresponding updated list of references for experimentally determined properties is presented.

CONTENTS

1. INTRODUCTION

This project is concerned with experimentally known small molecules, composed of the atoms H up to Ar. Special attention is paid to diatomic molecules where numerous experimentally determined properties are available for comparison with calculated data. The preselected set of 18 atoms gives rise in principle to 171 distinct neutral diatomic molecules. Consideration of the corresponding cations and anions, ignoring any possible excited states, would yield a grand total of some 500 basic molecular systems. Most of these, however, are still hypothetical, since only a subset, which comprises 214 systems out of these basic diatomics, has been observed hitherto. The entire subset of these species for which there is experimental evidence has been calculated uniformly at the B3LYP/cc-pvqz level of density functional theory, and the evaluated properties are compared with the corresponding available experimental values. The presentation of the results is similar to that in the book of Huber and Herzberg [1].

This project is intended to serve a threefold aim. On one hand, the predictive power of recently developed quantum chemical methods will be demonstrated, using the experimental data as a gauge. On the other hand, it will be shown that the calculated properties are very useful to complete our knowledge of these diatomic systems, for which there exists merely inchoate experimental information. Finally, carefully updated sets of experimentally detected molecular properties are presented, irrespective of the theoretical interests of the user. Most importantly, statistics are presented for the accuracy of the respective calculated molecular properties without the omission of computationally difficult molecules.

2. MOLECULAR PROPERTIES, SYMBOLS, AND UNITS

The set of 214 diatomic molecules splits into 76 closed-shell and 138 open-shell molecules. The set of 138 open-shell systems splits into 92 radicals with a doublet ground state and 46 radicals with higher spin multiplicities (triplet, quartet, quintet) in their ground states. From the set of 214 diatomic molecules, 102 are neutral species, 73 are cations, and 39 are anions. From 73 cations, 50 are radical cations; from 39 anions, 18 are radical anions. For 20 diatomic systems, low-lying electronic states were calculated. A set of 21 experimentally known noble gas (He, Ne, Ar) diatomic molecules were calculated. This situation represents a challenge for experimental as well as computational methods. Electronic states and their symmetry symbols, including the spin multiplicity, are important non-numerical features of molecules. For molecular systems like CO, N_2, O_2, the ground states of which have been unequivocally assigned, experimental as well as computed data are restricted to this single electronic state. In ambiguous cases, where low-lying electronic states are expected, several conceivable states have been investigated. This procedure provides not only the identification of experimentally unknown ground states (AlO^+), but also confirms (LiO) or rebuts (C_2^+) previous tentative assignments of the respective lowest-lying states. It should be noted, however, that the density functional approach fails to predict very weakly bound diatomic van der Waals-complexes such as He_2 or Ne_2, which require a thorough description of dispersion forces. A few exceptional molecules like B_2, C_2, and MgO need multi-configuration wave functions to establish the correct ground states. For dubious cases, *ab initio* ACPF (averaged coupled pair functional) calculations are recommended for a correct sequence of closely spaced (0.1 eV) electronic states. However, improved computational methods, for example, the widely used coupled cluster CCSD(T) method or the multireference ACPF approach, combined with extended basis sets, are much more time-consuming (for diatomic molecules a factor of 10 compared with the B3LYP method). The advantage of the B3LYP procedure, chosen for this project, is its recognized success as well as its ability to extend the range of application to systems up to 10 heavy atoms and to investigate hundreds of systems in reasonable time.

Relative term values T_e, referring to the ground state ($T_e = 0$), are the differences of total electronic minimum energies at the equilibrium geometries divided by the Planck constant and the speed of light and are given in cm^{-1}. The equilibrium internuclear distance r_e, the harmonic vibrational wave number ω_e, the vibrational absolute absorption intensity A, and the electric dipole moment μ are given in units of ångström (Å), cm^{-1}, km mol^{-1}, and debye (D), respectively (see the attached glossary). The sign of the dipole moment is positive for A^-B^+ and negative for A^+B^-. Calculated dipole moments carry either a *plus* or a *minus* sign, or are zero by symmetry. For most of the experimental dipole moments no signs are available. Few exceptions are CN, CO, ClF, and SiS. All calculated dipole moments are μ_e values. The origin of the dipole moment of ionic systems is chosen as the center of mass. Adiabatic ionization energies (E_i) are corrected for zero-point vibrations and are given in eV. Ionization energies have been calculated only if there exist an experimental E_i and/or the ionized species has been detected experimentally. The dissociation energy D_0(eV) of a molecule refers to the separated atoms in their respective ground states, and is corrected for zero-point energy. The separated atoms for ionic systems are indicated in parentheses. For AB^+ the lowest dissociation energy $D_0(A+B^+)$ is adopted if $E_i(A) > E_i(B)$. Therefore, Table 1 with atomic energies and ionization energies is attached to facilitate the identification of the pertinent asymptotes in these cases. Experimental atomic data are taken from the JANAF or Moore's tables [2], or from Bowers [3].

The information about diatomic molecules is summarized in Tables 2 and 3. Separate tables (Tables 7a–h) are given for comparison of experimental and calculated NMR chemical shifts δ (ppm) for the most abundant nuclei of 50 diatomic and small polyatomic molecules. Table 6 compares calculated and experimental anharmonicities, $\omega_e x_e$ (cm^{-1}), for 32 diatomic molecules. Experimental and calculated isotropic hyperfine coupling constants, i.e., Fermi contact parameters, A_{iso} (G) are compared in Table 4 for 12 diatomic and 8 polyatomic molecules of size up to the benzyl radical. And in Table 5 the calculated structures of 53 polyatomic molecules up to the size of SF_6 are compared with experimental structures from MW (microwave spectroscopy) or ED (electron diffraction).

Glossary

Symbol	Description	Unit
E	Total electronic ground-state energy	E_h (hartree)
State	Irreducible representation of the symmetry group	
T_e	Relative electronic energy referred to the ground state	cm^{-1}
r_e	Equilibrium internuclear distance	Å (ångström)
ω_e	Harmonic vibrational wavenumber	cm^{-1}
$\omega_e x_e$	Anharmonicity of vibrations	cm^{-1}
A	Vibrational absolute absorption intensity	km mol^{-1}
μ	Electric dipole moment	D (debye)
E_i	Adiabatic, zero-point energy corrected ionization energy	eV
D_0	Dissociation energy, corrected for zero-point energy	eV
δ	NMR (nuclear magnetic resonance) chemical shift	ppm
σ	NMR absolute shielding	ppm
A_{iso}	Isotropic hyperfine coupling constant	G (gauss)

Conversion of units

Length	$1\ \text{Å} \triangleq 10^{-10}\ \text{m} \triangleq 1.889726\ a_o$
Energy	$1\ E_h \triangleq 27.2114\ \text{eV} \triangleq 219474.63\ \text{cm}^{-1} \triangleq 627.510\ \text{kcal mol}^{-1} \triangleq 2625.500\ \text{kJ mol}^{-1}$
Dipole moment (electric)	$1\ \text{D} \triangleq 3.33564 \times 10^{-30}\ \text{Cm}$
Absorption intensity	$1\ \text{km mol}^{-1} \triangleq 4.062176\ \text{cm}^{-2}\ \text{atm}^{-1}$ at 300 K
Isotropic hyperfine coupling constant	$1\ \text{G} \triangleq 2.8025\ \text{MHz}$

From *Quantities, Units, and Symbols in Physical Chemistry*, 2nd ed., I. Mills, T. Cvitaš, K. Homann, N. Kallay and K. Kuchitsu, Blackwell Scientific Publications, Oxford (1993) [4].

3. COMPUTATIONAL PROCEDURES

The calculations were carried out using the GAUSSIAN 94 package of programs [5]. The computational method is Becke's gradient-corrected exchange-correlation density functionals (B3LYP) [6]. The unrestricted open-shell Hartree–Fock (UHF) formalism was applied to open-shell systems. According to the theorem of Hohenberg and Kohn [7], the functionals employed by DFT methods partition the electronic energy E of a molecule into the terms

$$E(\rho) = E^{\mathrm{T}}(\rho) + E^{\mathrm{V}}(\rho) + E^{\mathrm{J}}(\rho) + E^{\mathrm{XC}}(\rho)$$

where E^{T} is the kinetic energy of the electrons, E^{V} is the potential energy of nuclear–electron attraction and nuclear–nuclear repulsion, E^{J} is the electron–electron repulsion of the classical energy of the density ρ, and E^{XC} is the exchange energy (X) arising from the wave function including the dynamical correlation (C) of electron motion. The term E^{XC} is divided into two separate functionals

$$E^{\mathrm{XC}}(\rho) = E^{\mathrm{X}}(\rho) + E^{\mathrm{C}}(\rho)$$

The definition of the functionals $E^{\mathrm{X}}(\rho)$ and $E^{\mathrm{C}}(\rho)$ can be found in the literature (Foresman, Frisch [8]). Becke introduced a gradient-corrected functional $E^{\mathrm{X}}(\mathrm{B})(\rho,\nabla\rho)$ and formulated functionals which include a mixture (hybrid) of Hartree–Fock (HF) exchange and DFT exchange (X) plus correlation (C) as

$$E^{\mathrm{XC}}(\mathrm{hybrid}) = \mathrm{c}_{\mathrm{HF}}E^{\mathrm{X}}(\mathrm{HF}) + \mathrm{c}_{\mathrm{DFT}}E^{\mathrm{XC}}(\mathrm{DFT})$$

where the coefficients c are adjustable parameters. Becke's B3LYP functional, for instance, is a three-parameter functional of the following composition:

$$E^{\mathrm{XC}}(\mathrm{B3LYP}) = E^{\mathrm{X}} + \mathrm{c}_0[E^{\mathrm{X}}(\mathrm{HF}) - E^{\mathrm{X}}(\mathrm{DFT})] + \mathrm{c}_{\mathrm{X}}E^{\mathrm{X}}(\mathrm{B}) + E^{\mathrm{C}}(\mathrm{VWN3}) + \mathrm{c}_{\mathrm{C}}[E^{\mathrm{C}}(\mathrm{LYP}) - E^{\mathrm{C}}(\mathrm{VWN3})]$$

where VWN is the Vosko, Wilk, Nusair functional [9], and LYP is the Lee, Yang, Parr functional [10]. The parameters c_0, c_{X}, and c_{C} are determined by fitting to atomization energies, ionization energies, proton affinities, and atomic energies of a set of molecules. Thus, the B3LYP procedure is semi-empirical in this sense. DFT calculations proceed in the same way as *ab initio* HF calculations, with the addition of the extra term E^{XC}, which is computed via numerical integration.

A geometry optimization is complete when the force between the nuclei is below the cutoff value of 0.00045 $E_{\mathrm{h}}a_{\mathrm{o}}^{-1}$, and the calculated displacement of the internuclear distance for the next optimization step is below 0.0018 a_{o}. For weakly bound systems, scanning of the energy curve was applied in addition.

Vibrational wave numbers depend on second derivatives of the energy with respect to the nuclear positions. Analytic second derivatives are available for DFT calculations. The absolute absorption intensity A which is measured in the unit of km mol^{-1} is calculated by the formula

$$A_{1\text{-}0} = (8\pi^3/3\mathrm{hc})N_{\mathrm{A}}|\mu_{1\text{-}0}|^2\omega_{1\text{-}0}$$

where N_{A} is the Avogadro constant, $\mu_{1\text{-}0}$ is the electric dipole transition moment between the states 0 and 1, and $\omega_{1\text{-}0}$ is the wave number. In the experimental literature, the quantity $S = A/RT$ which is measured in the unit of cm^{-2}atm^{-1} at a given temperature T is used for gases. This quantity results from the substitution of the concentration c in Beer's law by the partial pressure p. The conversion of units is given above.

4. BASIS SETS

The Gaussian atomic basis sets cc-pvqz (correlation consistent polarized valence quadruple-zeta) [11] are used for the atoms H to Ar. The description of the basis sets is arranged line by line in the following way: atom, basis set key word, standard notation of the basis set, contraction scheme of the basis set, size of the basis set.

H cc-pvqz 4s/3p/2d/1f 6.1.1.1/1.1.1/1.1/1 35/30	He cc-pvqz 4s/3p/2d/1f 7.1.1.1/1.1.1/1.1/1 36/30	Li - Ne cc-pvqz 5s/4p/3d/2f/1g 12.12.1.1.1/6.1.1.1/1.1.1/1.1/1 92/55
Na - Ar cc-pvqz 6s/5p/3d/2f/1g 16.16.16.1.1.1/11.11.1.1.1/1.1.1/1.1/1 164/59		

Augmented basis sets (aug-cc-pvqz) were used for anionic systems of the type A^- (atomic anions), the results of which are listed in Table 1, and AH^- (diatomic hydrides). The key word aug-cc-pvqz results in additional diffuse functions of the type one s, one p set, one d set, etc. Augmented basis sets are not mentioned in Table 3 for diatomic molecules; instead, their use for $E_i(AH^-)$ is emphasized here. Augmented basis sets are also necessary, according to Table 1 for atoms, for $D_0(AB^-)$ where one of the dissociating atoms is either O^- or F^-.

Table 1 Total electronic energies E / E_h and ionization energies E_i / eV of the atoms H – Ar and their stable anions.

Atom	State	E(cc-pvqz)	E(aug-cc-pvqz)	E_i(calc.)	E_i(exp.)
H	^{2}S	–0.502346*	–0.502391	13.67	13.61
H^-	^{1}S	–0.517503	–0.535949*	0.91	0.75
He	^{1}S	–2.914981		24.94	24.59
He^+	^{2}S	–1.998484			
Li	^{2}S	–7.492222		5.62	5.39
Li^+	^{1}S	–7.285508			
Li^-	^{1}S	–7.509870		0.48	0.62
Be	^{1}S	–14.672628		9.11	9.32
Be^+	^{2}S	–14.337861			
Be^-	^{2}P	–14.654534		–	–
B	^{2}P	–24.664786		8.74	8.30
B^+	^{1}S	–24.343692			
B^-	^{3}P	–24.670391		0.15	0.28
C	^{3}P	–37.860591*	–37.860785	11.54	11.26
C^+	^{2}P	–37.436638			
C^-	^{4}S	–37.898495	–37.911284*	1.37	1.27
N	^{4}S	–54.605328*	–54.605735	14.65	14.54
N^+	^{3}P	–54.066941			
O	^{3}P	–75.098193*	–75.099041	14.12	13.61
O^+	^{4}S	–74.579257			
O^-	^{2}P	–75.136450	–75.160853*	1.68	1.46
F	^{2}P	–99.772525*	–99.773643	17.70	17.42

(*Continued on next page*)

Table 1 (*Continued*)

Atom	State	E(cc-pvqz)	E(aug-cc-pvqz)	E_i(calc.)	E_i(exp.)
F^+	^3P	–99.121972			
F^-	^1S	–99.877807	–99.903238*	3.53	3.40
Ne	^1S	–128.975664*	–128.977143	21.67	21.56
Ne^+	^2P	–128.179076			
Na	^2S	–162.298962		5.43	5.14
Na^+	^1S	–162.099313			
Na^-	^1S	–162.319312		0.58	0.55
Mg	^1S	–200.098962		7.73	7.65
Mg^+	^2S	–199.815032			
Mg^-	^2P, ^2S	–200.085222		–	–
Al	^2P	–242.393290*	–242.393323	6.02	5.99
Al^+	^1S	–242.171973			
Al^-	^3P	–242.403407	–242.410353*	0.46	0.44
Si	^3P	–289.399119*	–289.399169	8.11	8.15
Si^+	^2P	–289.100932			
Si^-	^4S	–289.443146	–289.448567*	1.34	1.39
P	^4S	–341.288711*	–341.288791	10.39	10.49
P^+	^3P	–340.907043			
P^-	^3P	–341.315305	–341.324065*	0.96	0.75
S	^3P	–398.142105*	–398.142260	10.55	10.36
S^+	^4S	–397.754305			
S^-	^2P	–398.215963	–398.223216*	2.20	2.08
Cl	^2P	–460.178519*	–460.178678	13.06	12.97
Cl^+	^3P	–459.698367			
Cl^-	^1S	–460.307494	–460.313669*	3.67	3.62
Ar	^1S	–527.563508*	–527.563658	15.79	15.76
Ar^+	^2P	–526.983284			

*Total energy used for E_i

5. STATISTICS OF DEVIATIONS BETWEEN CALCULATED AND EXPERIMENTAL PROPERTIES OF DIATOMIC MOLECULES

For N comparisons of calculated with experimental values of a property p, the mean absolute deviation

$$\overline{|\Delta p|} = \Sigma_i^N |\Delta p_i|/N = \Sigma_i^N |p_i(\text{calc.}) - p_i(\text{exp.})|/N$$

the average value

$$\bar{p} = \Sigma_i^N p_i/N$$

and the mean relative deviation

$$\overline{|\Delta p|}/\bar{p}$$

are listed in Table 2.

The statistics for equilibrium internuclear distances r_e and harmonic vibrational wave numbers ω_e incorporates data for electronic ground states. The statistics for r_e and ω_e, presented in Table 2, are more successful than those for *ab initio* HF and MP2 (Moeller–Plesset second-order perturbation theory) calculations of the literature (Hehre *et al.* [12]). Statistics of the past, however, suffer from limited numbers of comparisons and also from the omission of worst cases. Even more successful are the present

Table 2 Statistics for properties of diatomic molecules. N: number of comparisons between calculated and experimental values of property p; $\overline{|\Delta p|}$: mean absolute deviation; $\bar{p}$: average value of calculated data; $\overline{|\Delta p|}/\bar{p}$: mean relative deviation; $|\Delta p|$(max.): maximum absolute deviation between calculated and experimental value of property p.

N	$\overline{\lvert\Delta r_e\rvert}$	$\bar{r}_e$	$\overline{\lvert\Delta r_e\rvert}/\bar{r}_e$	$\lvert\Delta r_e\rvert$(max.)
138	0.0125 Å	1.5994 Å	0.0078	0.0645 Å (He_2^+)
N	$\overline{\lvert\Delta \omega_e\rvert}$	$\bar{\omega}_e$	$\overline{\lvert\Delta \omega_e\rvert}/\bar{\omega}_e$	$\lvert\Delta \omega_e\rvert$(max.)
133	40 cm^{-1}	1430 cm^{-1}	0.0282	338 cm^{-1} (He_2^+)
N	$\overline{\lvert\Delta \mu\rvert}$	$\bar{\mu}$	$\overline{\lvert\Delta \mu\rvert}/\bar{\mu}$	$\lvert\Delta \mu\rvert$(max.)
40	0.17 D	2.35 D	0.0746	0.94 D (NaH)
N	$\overline{\lvert\Delta E_i\rvert}$	$\bar{E}_i$	$\overline{\lvert\Delta E_i\rvert}/\bar{E}_i$	$\lvert\Delta E_i\rvert$(max.)
50[a]	0.19 eV	10.41 eV	0.0179	1.02 eV (LiMg)
5[b]	0.78 eV	29.46 eV	0.0265	2.08 eV (N_2^+)
38[c]	0.17 eV	1.41 eV	0.1204	0.70 eV (C_2^-)
N	$\overline{\lvert\Delta D_0\rvert}$	$\bar{D}_0$	$\overline{\lvert\Delta D_0\rvert}/\bar{D}_0$	$\lvert\Delta D_0\rvert$(max.)
155	0.17 eV	3.86 eV	0.0433	1.23 eV (Ne_2^+)
N	$\overline{\lvert\Delta \omega_e x_e\rvert}$	$\overline{\omega_e x_e}$	$\overline{\lvert\Delta \omega_e x_e\rvert}/\overline{\omega_e x_e}$	$\lvert\Delta \omega_e x_e\rvert$(max.)
31	2.56 cm^{-1}	37.8 cm^{-1}	0.0677	7.35 cm^{-1}(NH)

[a] neutral molecules, [b] cations, [c] anions

statistics for dissociation energies D_0 which overrule in some sense the skepticism as exemplified by the remark of Benson [13] in 1981: "*Ab initio* methods for solving the Schrödinger equation are not yet capable of providing results of $\Delta_f H$ to better than ±4 kcal mol^{-1} even for relatively simple species and the prospect is not bright for any major breakthroughs in this area in the next decade or so". (See for comparison in Table 2: $\overline{|\Delta D_0|}$ = 0.17 eV = 3.8 kcal mol^{-1})[*]. No statistics are presented for absorption intensities A owing to the limited number of only five comparisons.

In view of the combined theoretical and experimental uncertainties, the following aspect should be taken into account. If there is a discrepancy between a calculated and experimental value, there is always a possibility that it is the latter that is in error. Famous resolved examples are CH^- and SiH^-, or SiCl and SiF. The cation $HeNe^+$, for instance, which is excluded from the statistics, is an unresolved example where data from calculations [B3LYP and CCSD(T)] differ dramatically from uncertain experimental data. Uncertain experimental properties are set in parentheses and are generally not considered in the present statistics.

Statistics can be found in the literature where the G2 procedure was employed. G2 is not a computational method but a series of *ab initio* calculations, including empirical corrections, to use the additivity of basis set extension and the extension of electron correlation for the total electronic energy. The application is, therefore, restricted to the properties E_i and D_0. The limited number of diatomic systems, 25(E_i) and 26(D_0), makes statistics questionable [14]. The G2 procedure was applied also to small molecules, 42(E_i) and 56(D_0). For both properties, mean absolute deviations of 0.05 eV were reported. However, worst cases were omitted, such as C_2^-(0.44), CN(0.42), LiMg(1.23) for E_i (absolute deviations in eV in parentheses), and CCl(0.82), MgO(0.96) for D_0 (absolute deviations in eV in parentheses) [15]. A variety of *ab initio* methods was applied to 120 first- and second-row diatomic molecules where the properties T_e, r_e, ω_e, and D_0 are presented; however, ions as well as rare gas compounds were omitted [16].

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[*] 1 kcal ≙ 4.184 kJ

Recently performed statistics from the literature for r_e, ω_e, E_i, and D_0 still suffer from the limited sets of data, but the comparison with different DFT methods globally favors the B3LYP method [17]. The G2 procedure for the calculation of E_i and D_0 was very recently replaced by G3 where the B3LYP method is involved [18]. No statistics could be found in the literature for anharmonicities, $\omega_e x_e$, NMR chemical shifts, δ, for the most abundant nuclei, dipole moments, μ, and isotropic hyperfine coupling constants A_{iso}.

6. TABLE OF PROPERTIES OF DIATOMIC MOLECULES

Table 3 for properties of diatomic molecules is arranged as follows. Calculated data can be found in the lines with the boldface molecular formulae on the far left. These lines have a blank space in the far right column, indicated by Ref.(Exp.). The corresponding following lines with one or more reference numbers on the outer right show experimental values. In some cases, electronically excited states were calculated, in addition to the ground state. One line is used per state for calculated as well as experimental data (cf., for example, CH). Sometimes, in particular for cations AB$^+$, there is a full blank line instead of experimental values. In such a case, the ionization energy (E_i) of the corresponding neutral compound AB is experimentally known, and therefore, the cation AB$^+$ is regarded as an identified diatomic system (cf., for example, AlF$^+$), irrespective of additional known properties. Uncertain experimental properties are set in parentheses (cf., for example, Cl$_2^-$).

Table 3 B3LYP calculated and experimental properties of diatomic molecules for H – Ar. T_e / cm^{-1}: relative electronic energy referred to the ground state; r_e / Å: equilibrium internuclear distance; ω_e / cm^{-1}: harmonic vibrational wavenumber; A / km mol^{-1}: vibrational absolute absorption intensity; μ / D: electric dipole moment; E_i / eV: adiabatic, zero-point energy corrected ionization energy; D_0 / eV: dissociation energy, corrected for zero-point energy. For conversion of units see chapter 2.

Molecule	State	T_e	r_e	ω_e	A	μ	E_i	D_0	Ref.(Exp.)
$^{27}Al_2$	$^3\Sigma_g^-$	0	2.5020	324	0	0		1.20	
	$^3\Sigma_g^-$	0	2.466	350				1.34	1,19
$^{27}Al_2^-$	$^2\Sigma_u^-$	0	2.4493	345	0	0	0.81	1.74	
							1.10		19
$^{27}Al^{35}Cl$	$^1\Sigma^+$	0	2.1619	458	126	–1.77	9.26	5.04	
	$^1\Sigma^+$	0	2.1301	481		1.5 ± 0.5	9.4	5.26	1,19
$^{27}Al^{35}Cl^+$	$^2\Sigma^+$	0	2.0368	577	60	–5.62		1.81(Al$^+$ + Cl)	
									19
$^{27}Al^{19}F$	$^1\Sigma^+$	0	1.6735	780	108	–1.55	9.73	6.88	
	$^1\Sigma^+$	0	1.6544	802		1.53	9.73	6.84	1,19
$^{27}Al^{19}F^+$	$^2\Sigma^+$	0	1.6113	925	79	–5.35		3.18(Al$^+$ + F)	
									1
$^{27}Al^1H$	$^1\Sigma^+$	0	1.6599	1653	704	–0.20	8.23	3.06	
	$^1\Sigma^+$	0	1.6474	1682		0.32		2.91	19,20
$^{27}Al^1H^+$	$^2\Sigma^+$	0	1.6198	1632	22	–0.62		0.85(Al$^+$ + H)	
	$^2\Sigma^+$	0	1.6018	1620					1
$^{27}Al^{14}N$	$^3\Pi$	0	1.7920	748	9	–2.80		2.73	
	$^3\Pi$	0	1.7864	747				3.04 ± 1.0	1,19
$^{27}Al^{16}O$	$^2\Sigma^+$	0	1.6290	955	1	–4.21	9.86	5.16	
	$^2\Sigma^+$	0	1.6179	979			9.53	5.27	1
$^{27}Al^{16}O^+$	$^1\Sigma^+$	3815	1.6035	1008	2	–7.17			
	$^3\Pi$	0	1.7459	738	12	–4.59		1.32(Al$^+$ + O)	
									1
$^{27}Al^{16}O^-$	$^1\Sigma^+$	0	1.6425	981	59	–1.16	2.44	6.55(Al + O$^-$)	
							2.60		19
$^{27}Al^{31}P$	$^3\Pi$	0	2.2234	456	8	–2.48		2.25	

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Table 3 (*Continued*)

Molecule	State	T_e	r_e	ω_e	A	μ	E_i	D_0	Ref.(Exp.)
								2.21 ± 0.1	1,19
$^{27}\mathrm{Al}^{32}\mathrm{S}$	$^2\Sigma^+$	0	2.0460	593	14	–3.85		4.04	
	$^2\Sigma^+$	0	2.029	617				3.84	1
$^{27}\mathrm{Al}^{32}\mathrm{S}^-$	$^1\Sigma^+$	0	2.1046	563	73	–0.16	2.58	4.61(Al + S^-)	
							2.60		19
$^{27}\mathrm{Al}^{28}\mathrm{Si}$	$^4\Sigma^-$	0	2.4317	364	11	–1.35		2.37	
								2.34	1
$^{40}\mathrm{Ar}_2$	$^1\Sigma_g^+$	(repulsive potential)							
	$^1\Sigma_g^+$	0	3.758	26 (ω_0)				0.01	1
$^{40}\mathrm{Ar}_2^+$	$^2\Sigma_u^+$	0	2.5419	222	0	0		1.86	
	$^2\Sigma_u^+$	0						≥1.05; 1.30	1
$^{40}\mathrm{Ar}^{19}\mathrm{F}$	$^2\Sigma^+$	0	2.5596	106	5	–0.62	13.69	0.033	
									1
$^{40}\mathrm{Ar}^{19}\mathrm{F}^+$	$^1\Sigma^+$	0	1.6276	760	0	–1.55		2.13(Ar^+ + F)	
	$^1\Sigma^+$	0	1.621	719		1.5		2.09	1,21
$^{40}\mathrm{Ar}^{1}\mathrm{H}^+$	$^1\Sigma^+$	0	1.2929	2625	536	+2.00		3.91(Ar + H^+)	
	$^1\Sigma^+$	0	1.280	2711		1.4		4.01	1,22–24
$^{40}\mathrm{Ar}^{16}\mathrm{O}$	$^3\Pi$	0	3.4498	25	0	–0.04		0.0003 (D_e 0.002)	
			(3.31)					0.01 (D_e)	1
$^{11}\mathrm{B}_2$	$^3\Sigma_g^-$	1450	1.6111	1005	0	0			
	$^5\Sigma_u^+$	0	1.5146	1282	0	0		2.71	
	$^3\Sigma_g^-$	0	1.590	1051				3.04 ± 0.2	1,19
$^{11}\mathrm{B}^{12}\mathrm{C}$	$^4\Sigma^-$	0	1.4812	1194	26	–1.27		4.42	
								4.60 ± 0.3	1,19
$^{11}\mathrm{B}^{35}\mathrm{Cl}$	$^1\Sigma^+$	0	1.7218	821	231	+1.57		5.10	
	$^1\Sigma^+$	0	1.7153	829				5.26	1,19,25
$^{9}\mathrm{Be}_2$	$^1\Sigma_g^+$	0	2.4824	286	0	0		0.17	
	$^1\Sigma_g^+$	0	2.45	276	0	0		0.10	26
$^{9}\mathrm{Be}^{40}\mathrm{Ar}^+$	$^2\Sigma^+$	0	2.1199	344	269	–4.23		0.57(Be^+ + Ar)	
	$^2\Sigma^+$	0	2.085	369					1
$^{9}\mathrm{Be}^{35}\mathrm{Cl}$	$^2\Sigma^+$	0	1.8019	831	124	–0.91		4.10	
	$^2\Sigma^+$	0	1.7971	847				3.99 ± 0.1	1,19
$^{9}\mathrm{Be}^{19}\mathrm{F}$	$^2\Sigma^+$	0	1.3626	1262	113	–1.17		6.11	
	$^2\Sigma^+$	0	1.3610	1247				5.94 ± 0.4	1,19
$^{9}\mathrm{Be}^{1}\mathrm{H}$	$^2\Sigma^+$	0	1.3400	2063	139	–0.30	8.50	2.39	
	$^2\Sigma^+$	0	1.3426	2061			8.21	2.03	1
$^{9}\mathrm{Be}^{1}\mathrm{H}^+$	$^1\Sigma^+$	0	1.3129	2212	56	–3.52		3.00(Be^+ + H)	
	$^1\Sigma^+$	0	1.3122	2222				3.14	1
$^{9}\mathrm{Be}^{1}\mathrm{H}^-$	$^1\Sigma^+$	0	1.4315	1588	1148	–3.98	0.38	1.87(Be + H^-)	
	$^1\Sigma^+$	0					0.7	1.94	27
$^{9}\mathrm{Be}^{16}\mathrm{O}$	$^1\Sigma^+$	0	1.3193	1554	12	–6.27	9.92	4.73	
	$^1\Sigma^+$	0	1.3309	1487			(10.1 ± 0.4)	4.47 ± 0.1	1,19
$^{9}\mathrm{Be}^{16}\mathrm{O}^+$	$^2\Sigma^+$	9137	1.3372	1438	278	–6.54			
	$^2\Pi$	0	1.4160	1280	138	–7.57		3.96(Be^+ + O)	
									19
$^{9}\mathrm{Be}^{32}\mathrm{S}$	$^3\Pi$	5854	1.9151	740	77	–0.65			
	$^1\Sigma^+$	0	1.7378	1014	18	–5.32		3.39	
	$^1\Sigma^+$	0	1.7415	998				3.82 ± 0.6	1,19
$^{11}\mathrm{B}^{19}\mathrm{F}$	$^1\Sigma^+$	0	1.2611	1406	146	+0.99	11.02	7.76	
	$^1\Sigma^+$	0	1.2627	1402		0.5 ± 0.2	11.12	7.81	1,28
$^{11}\mathrm{B}^{19}\mathrm{F}^+$	$^2\Sigma^+$	0	1.2115	1692	176	–3.46		5.47(B^+ + F)	
									1
$^{11}\mathrm{B}^{1}\mathrm{H}$	$^1\Sigma^+$	0	1.2313	2350	404	+1.56	9.70	3.49	
	$^1\Sigma^+$	0	1.2324	2367		1.27	9.77	3.49	1,19
$^{11}\mathrm{B}^{1}\mathrm{H}^+$	$^2\Sigma^+$	0	1.2022	2536	66	–0.11		2.53(B^+ + H)	

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Table 3 (*Continued*)

Molecule	State	T_e	r_e	ω_e	A	μ	E_i	D_0	Ref.(Exp.)
	$^2\Sigma^+$	0	1.2147 (r_0)					1.95	1
$^{11}\mathrm{B}^{14}\mathrm{N}$	$^3\Pi$	0	1.3164	1570	0	–0.90		4.76	
	$^3\Pi$	0	1.281	1515				3.99 ± 0.2	1,19,29
$^{11}\mathrm{B}^{16}\mathrm{O}$	$^2\Sigma^+$	0	1.2000	1921	46	–2.38	13.22	8.36	
	$^2\Sigma^+$	0	1.2045	1886				8.34 ± 0.2	1,19
$^{11}\mathrm{B}^{16}\mathrm{O}^+$	$^1\Sigma^+$	0	1.1867	1949	3	–5.94		3.87(B^+ + O)	
	$^1\Sigma$	0	(1.2052)	(1787)					1
$^{11}\mathrm{B}^{16}\mathrm{O}^-$	$^1\Sigma^+$	0	1.2323	1748	75	+2.43	2.46	9.11(B + O^-)	
							2.84		30
$^{11}\mathrm{B}^{31}\mathrm{P}$	$^3\Pi$	0	1.7417	956	5	–0.17		3.47	
								3.56 ± 0.2	1,19
$^{11}\mathrm{B}^{32}\mathrm{S}$	$^2\Sigma^+$	0	1.6100	1183	40	–0.86		5.68	
	$^2\Sigma^+$	0	1.6092	1180				5.98 ± 0.1	1,19
$^{11}\mathrm{B}^{28}\mathrm{Si}$	$^4\Sigma^-$	0	1.9134	744	2	+0.65		3.23	
								3.24	1,19
$^{12}\mathrm{C}_2$	$^1\Sigma_g{}^+$	8005	1.2458	1876	0	0			
	$^3\Pi_u$	0	1.3005	1692	0	0	11.90	6.09	
	$^3\Pi_u$	716	1.3119	1641					1
	$^1\Sigma_g{}^+$	0	1.2425	1855			12.15	6.21	1
$^{12}\mathrm{C}_2{}^+$	$^2\Pi_u$	11304	1.3164	1594	0	0			
	$^4\Pi_u$	8593	1.2418	2002	0	0			
	$^4\Sigma_g{}^-$	0	1.4027	1333	0	0		5.73	
	$^2\Pi_u$	(?)	(1.301)	(1350)				5.32	1
$^{12}\mathrm{C}_2{}^-$	$^2\Sigma_g{}^+$	0	1.2554	1854	0	0	4.24	8.29	
	$^2\Sigma_g{}^+$	0	1.2682	1781			3.54	8.48	1
$^{12}\mathrm{C}^{35}\mathrm{Cl}$	$^2\Pi$	0	1.6600	849	132	+1.43	9.10	4.14	
	$^2\Pi$	0	1.6452	877			9.05	(3.34)	1,31,32
$^{12}\mathrm{C}^{35}\mathrm{Cl}^+$	$^1\Sigma^+$	0	1.5416	1171	214	+0.22		6.58(C^+ + Cl)	
	$^1\Sigma$	0	1.538	1175					1,32
$^{12}\mathrm{C}^{35}\mathrm{Cl}^-$	$^3\Sigma^-$	0	1.9085	457	64	+3.35	1.17	1.80(C + Cl^-)	
							0.89 ± 0.2		32
$^{12}\mathrm{C}^{19}\mathrm{F}$	$^2\Pi$	0	1.2739	1296	185	+0.75	9.46	5.74	
	$^2\Pi$	0	1.2718	1308		0.65	9.11	5.67; 5.74	1,19,33
$^{12}\mathrm{C}^{19}\mathrm{F}^+$	$^1\Sigma^+$	0	1.1540	1791	203	–0.95		7.81(C^+ + F)	
			1.154						32
$^{12}\mathrm{C}^{19}\mathrm{F}^-$	$^3\Sigma^-$	0	1.4524	785	132	+3.06	0.35	2.53(C + F^-)	
							0.49 ± 0.15		32
$^{12}\mathrm{C}^{1}\mathrm{H}$	$^4\Sigma^-$	7340	1.0921	3050	50	+0.70			
	$^2\Pi$	0	1.1219	2827	149	+1.47	11.01	3.53	
	$^4\Sigma^-$	(5844)	(1.085)	(3145)					1
	$^2\Pi$	0	1.1181	2858		1.46	10.64	3.46	1
$^{12}\mathrm{C}^{1}\mathrm{H}^+$	$^1\Sigma^+$	0	1.1359	2802	1	+1.45		4.05(C^+ + H)	
	$^1\Sigma^+$	0	1.1309	2740 (ω_0)				4.08	1
$^{12}\mathrm{C}^{1}\mathrm{H}^-$	$^3\Sigma^-$	0	1.1447	2526	803	+1.47	1.37	3.55(C^- + H)	
	$^3\Sigma^-$	0	1.150	2620			1.24	3.44	1,27,34
$^{35}\mathrm{Cl}_2$	$^1\Sigma_g{}^+$	0	2.0173	540	0	0	11.37	2.34	
	$^1\Sigma_g{}^+$	0	1.9879	560			11.48	2.48	1,19
$^{35}\mathrm{Cl}_2{}^+$	$^2\Pi_g$	0	1.9158	632	0	0		4.04	
	$^2\Pi_g$	0	1.8915	645				3.95	1
$^{35}\mathrm{Cl}_2{}^-$	$^2\Sigma_u{}^+$	0	2.7167	199	0	0	2.74	1.58	
	$^2\Sigma_u{}^+$	0	(2.650)	(249)			2.39	1.26	1,35
							2.52	1.38 (D_e)	1,35
$^{35}\mathrm{Cl}^{19}\mathrm{F}$	$^1\Sigma^+$	0	1.6430	788	27	–0.93	12.58	2.56	
	$^1\Sigma^+$	0	1.6283	786		–0.89	12.66	2.62	1

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Table 3 (*Continued*)

Molecule	State	T_e	r_e	ω_e	A	μ	E_i	D_0	Ref.(Exp.)
$\mathbf{^{35}Cl^{19}F^{+}}$	$^2\Pi$	0	1.5466	931	25	–1.70		3.04(Cl$^+$ + F)	
	$^2\Pi$	0		870				2.93	1
				912					1
$\mathbf{^{35}Cl^{16}O}$	$^2\Pi$	0	1.5839	854	4	–1.33	10.88	2.77	
	$^2\Pi$	0	1.5696	854	2; 3	1.30	10.87	2.75	1,36
$\mathbf{^{35}Cl^{16}O^{+}}$	$^3\Sigma^-$	0	1.4848	1084	13	–1.27		4.95(Cl$^+$ + O)	
			1.480						36
$\mathbf{^{35}Cl^{16}O^{-}}$	$^1\Sigma^+$	0	1.7074	635	3	–2.37	1.97	1.23(Cl$^-$ + O)	
			1.673				2.28		36
$\mathbf{^{12}C^{14}N}$	$^2\Sigma^+$	0	1.1610	2154	21	–1.37	15.16	7.67	
	$^2\Sigma^+$	0	1.1718	2069		–1.45	14.17	7.76	1
$\mathbf{^{12}C^{14}N^{+}}$	$^1\Sigma^+$	0	1.1713	2080	1	–2.00		4.04(C$^+$ + N)	
	$^1\Sigma$	0	1.1729	2033				4.85	1
$\mathbf{^{12}C^{14}N^{-}}$	$^1\Sigma^+$	0	1.1692	2140	10	+0.59	3.88	10.52(C$^-$ + N)	
							3.82	10.31	1
$\mathbf{^{12}C^{16}O}$	$^1\Sigma^+$	0	1.1238	2215	77	+0.11	14.16	10.96	
	$^1\Sigma^+$	0	1.1283	2170	64	+0.12	14.01	11.09	1
$\mathbf{^{12}C^{16}O^{+}}$	$^2\Sigma^+$	0	1.1077	2296	13	–2.73	27.17	8.34(C$^+$ + O)	
	$^2\Sigma^+$	0	1.1151	2214			26.8	8.34	1
$\mathbf{^{12}C^{16}O^{++}}$	$^3\Pi$	0	1.2310	1559	28	–3.37		–4.72(C$^+$ + O$^+$)	
	$^3\Pi$	0							1
$\mathbf{^{12}C^{31}P}$	$^2\Sigma^+$	0	1.5538	1281	1	+1.04		5.25	
	$^2\Sigma^+$	0	1.562	1240				5.28	1
$\mathbf{^{12}C^{32}S}$	$^1\Sigma^+$	0	1.5338	1303	85	+1.93	11.42	7.10	
	$^1\Sigma^+$	0	1.5349	1285		1.96	11.33	7.35	1
$\mathbf{^{12}C^{32}S^{+}}$	$^2\Sigma^+$	0	1.4873	1411	17	–0.54		6.23(C + S$^+$)	
	$^2\Sigma^+$	0	1.4954	1384				6.38	1
$\mathbf{^{12}C^{32}S^{-}}$	$^2\Pi$	0	1.6348	989	39	+2.63	0.14	5.23(C + S$^-$)	
							0.20		19
$\mathbf{^{19}F_2}$	$^1\Sigma_g^+$	0	1.3966	1048	0	0	15.61	1.56	
	$^1\Sigma_g^+$	0	1.4119	917			15.69	1.60	1
$\mathbf{^{19}F_2^{+}}$	$^2\Pi_g$	0	1.2931	1232	0	0		3.65	
	$^2\Pi_g$	0	1.322	1073				3.34	1
$\mathbf{^{19}F_2^{-}}$	$^2\Sigma_u^+$	0	2.0187	353	0	0	3.33	1.34	
	$^2\Sigma_u^+$	0	(1.900)	(450)			3.08	1.28; (1.31)	1,35
$\mathbf{^{19}F^{16}O}$	$^2\Pi$	0	1.3486	1116	45	–0.03	12.84	2.36	
	$^2\Pi$	0	1.3541	1053	24	0.004	12.77	2.24 ± 0.1	1,19,36
$\mathbf{^{19}F^{16}O^{+}}$	$^3\Sigma^-$	0	1.2279	1403	57	+0.68		3.63(F + O$^+$)	
			1.234						36
$\mathbf{^{19}F^{16}O^{-}}$	$^1\Sigma^+$	0	1.5220	793	29	–1.31	1.94	0.74(F$^-$ + O)	
			1.516				2.27		36
$\mathbf{^{1}H_2}$	$^1\Sigma_g^+$	0	0.7419	4416	0	0	15.36	4.51	
	$^1\Sigma_g^+$	0	0.7414	4401			15.43	4.48	1
$\mathbf{^{1}H_2^{+}}$	$^2\Sigma_g^+$	0	1.1143	1997	0	0		2.82	
	$^2\Sigma_g^+$	0	1.052	2322				2.65	1
$\mathbf{^{1}H^{35}Cl}$	$^1\Sigma^+$	0	1.2820	2940	40	–1.15	12.72	4.36	
	$^1\Sigma^+$	0	1.2745	2991	17	1.11	12.75	4.43	1
$\mathbf{^{1}H^{35}Cl^{+}}$	$^2\Pi$	0	1.3250	2619	267	–1.55		4.70(H + Cl$^+$)	
	$^2\Pi$	0	1.3147	2674				4.65	1
$\mathbf{^{4}He_2}$	$^1\Sigma_g^+$	0	(repulsive potential)						
	$^1\Sigma_g^+$	0	2.97				22.22	0.0009 (D_e)	1
$\mathbf{^{4}He_2^{+}}$	$^2\Sigma_u^+$	0	1.1453	1360	0	0	36.75	3.27	
	$^2\Sigma_u^+$	0	1.0808	1698			37 ± 2	2.36	1,37
$\mathbf{^{4}He_2^{++}}$	$^1\Sigma_g^+$	0	0.7002	3512	0	0		–8.54(He$^+$ + He$^+$)	

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Table 3 (*Continued*)

Molecule	State	T_e	r_e	ω_e	A	μ	E_i	D_0	Ref.(Exp.)
									37
$^{4}\mathrm{He}^{40}\mathrm{Ar}$	$^{1}\Sigma^{+}$	0	(repulsive potential)						
	$^{1}\Sigma^{+}$	0	3.51					0.0024 (D_e)	1
$^{4}\mathrm{He}^{40}\mathrm{Ar}^{+}$	$^{2}\Sigma^{+}$	0	2.1236	329	24	+0.19		0.12(He + Ar^{+})	
									1
$^{4}\mathrm{He}^{1}\mathrm{H}^{+}$	$^{1}\Sigma^{+}$	0	0.7879	3073	776	+1.27		1.82(He + H^{+})	
	$^{1}\Sigma^{+}$	0	0.7743	2911		(1.66)		1.84	1,23
$^{4}\mathrm{He}^{20}\mathrm{Ne}$	$^{1}\Sigma^{+}$	0	(repulsive potential)						
	$^{1}\Sigma^{+}$	0	3.21					0.0002	1
$^{4}\mathrm{He}^{20}\mathrm{Ne}^{+}$	$^{2}\Sigma^{+}$	0	1.4970	808	0	–1.37		1.50(He + Ne^{+})	
	$^{2}\Sigma^{+}$	0	(1.300)	(1308)				(0.69)	1
$^{1}\mathrm{H}^{19}\mathrm{F}$	$^{1}\Sigma^{+}$	0	0.9214	4088	104	–1.82	16.01	5.76	
	$^{1}\Sigma^{+}$	0	0.9168	4138		1.83	16.04	5.87	1
$^{1}\mathrm{H}^{19}\mathrm{F}^{+}$	$^{2}\Pi$	0	1.0133	2986	541	–2.36		3.42(H^{+} + F)	
	$^{2}\Pi$	0	1.0011	3090				3.42	1
$^{7}\mathrm{Li}_2$	$^{1}\Sigma_g^{+}$	0	2.6910	345	0	0	5.23	0.98	
	$^{1}\Sigma_g^{+}$	0	2.6729	351			5.14	1.05	1,38
$^{7}\mathrm{Li}_2^{+}$	$^{2}\Sigma_g^{+}$	0	3.0623	251	0	0		1.28	
			3.12	262				1.30	38
$^{7}\mathrm{Li}_2^{-}$	$^{2}\Sigma_u^{+}$	0	3.0311	225	0	0	0.43	0.83	
								(0.88)	1
$^{7}\mathrm{Li}^{27}\mathrm{Al}$	$^{1}\Sigma^{+}$	0	2.8794	306	12	–2.66		0.89	
								0.75	19
$^{7}\mathrm{Li}^{40}\mathrm{Ar}^{+}$	$^{1}\Sigma^{+}$	0	2.3446	283	150	–8.25		0.31(Li^{+} + Ar)	
								0.30 (D_e)	1
$^{7}\mathrm{Li}^{9}\mathrm{Be}$	$^{2}\Pi$	4919	2.2328	502	40	–3.73			
	$^{2}\Sigma^{+}$	0	2.5600	351	11	–2.81		0.45	
	$^{2}\Sigma^{+}$		2.59(r_0)	295(ω_0)					39
$^{7}\mathrm{Li}^{35}\mathrm{Cl}$	$^{1}\Sigma^{+}$	0	2.0200	643	121	–6.90	9.80	4.73	
	$^{1}\Sigma^{+}$	0	2.0207	643		7.13	9.57	4.82 ± 0.1	1,19
$^{7}\mathrm{Li}^{35}\mathrm{Cl}^{+}$	$^{2}\Sigma^{+}$	4716	2.7873	109	163	–10.08			
	$^{2}\Pi$	0	2.3823	325	135	–7.97		0.55(Li^{+} + Cl)	
									19
$^{7}\mathrm{Li}^{35}\mathrm{Cl}^{-}$	$^{2}\Sigma^{+}$	0	2.1300	501	25	+7.35	0.63	1.85(Li + Cl^{-})	
	$^{2}\Sigma^{+}$	0	2.123	500			0.59	1.75	40
$^{7}\mathrm{Li}^{19}\mathrm{F}$	$^{1}\Sigma^{+}$	0	1.5609	915	140	–6.12		5.90	
	$^{1}\Sigma^{+}$	0	1.5639	910		6.28		5.94 ± 0.2	1,19
$^{7}\mathrm{Li}^{1}\mathrm{H}$	$^{1}\Sigma^{+}$	0	1.5900	1406	173	–5.70	7.93	2.45	
	$^{1}\Sigma^{+}$	0	1.5957	1406		5.88	7.7	2.43	1,19
$^{7}\mathrm{Li}^{1}\mathrm{H}^{+}$	$^{2}\Sigma^{+}$	0	2.1801	468	20	–1.91		0.16(Li^{+} + H)	
									19
$^{7}\mathrm{Li}^{1}\mathrm{H}^{-}$	$^{2}\Sigma^{+}$	0	1.6865	1145	715	+3.36	0.35	2.40(Li + H^{-})	
							0.34		19
$^{7}\mathrm{Li}^{4}\mathrm{He}^{+}$	$^{1}\Sigma^{+}$	0	1.8721	309	60	–3.31		0.08(Li^{+} + He)	
								0.07	32
$^{7}\mathrm{Li}^{24}\mathrm{Mg}$	$^{2}\Sigma^{+}$	0	3.0954	186	1	–0.57	4.94	0.18	
	$^{2}\Sigma^{+}$						5.96	0.66	19,41
$^{7}\mathrm{Li}^{24}\mathrm{Mg}^{+}$	$^{1}\Sigma^{+}$	0	2.8846	267	93	–5.68		0.86(Li^{+} + Mg)	
									41
$^{7}\mathrm{Li}^{14}\mathrm{N}$	$^{3}\Pi$	2015	1.7114	792	123	–5.70			
	$^{3}\Sigma^{-}$	0	1.8542	679	18	–6.64		1.89	
	$^{3}\Sigma^{-}$	0							2
$^{7}\mathrm{Li}^{23}\mathrm{Na}$	$^{1}\Sigma^{+}$	0	2.8758	254	0	+0.02	5.17	0.80	
	$^{1}\Sigma^{+}$	0	2.815	257		0.46	5.05	0.86	1,19
$^{7}\mathrm{Li}^{23}\mathrm{Na}^{+}$	$^{2}\Sigma^{+}$	0	3.3361	180	9	–4.32		1.05(Li + Na^{+})	

(*Continued on next page*)

Table 3 (*Continued*)

Molecule	State	T_e	r_e	ω_e	A	μ	E_i	D_0	Ref.(Exp.)
								0.99	1
$^{7}\mathrm{Li}^{16}\mathrm{O}$	$^{2}\Sigma^{+}$	2290	1.5858	871	166	–5.65			
	$^{2}\Pi$	0	1.6821	821	99	–6.39	8.80	3.70	
	$^{2}\Sigma^{+}$	2565							42
	$^{2}\Pi$	0	1.6882	815		6.84	8.45	3.42 ± 0.1	1,19,42
$^{7}\mathrm{Li}^{16}\mathrm{O}^{+}$	$^{3}\Sigma^{-}$	0	2.0736	365	94	–6.41		0.53(Li^{+} + O)	
									1
$^{7}\mathrm{Li}^{31}\mathrm{P}$	$^{3}\Sigma^{-}$	0	2.3249	490	25	–6.57		1.86	
	$^{3}\Sigma^{-}$							2.53 ± 0.24	41
$^{7}\mathrm{Li}^{32}\mathrm{S}$	$^{2}\Pi$	0	2.1500	576	81	–6.86		3.17	
								3.20; 3.37 ± 0.4	41
$^{7}\mathrm{Li}^{28}\mathrm{Si}$	$^{4}\Sigma^{-}$	0	2.3629	448	57	–5.79		1.63	
								1.54	41
$^{24}\mathrm{Mg}_2$	$^{1}\Sigma_g^{+}$	0	3.9478	47	0	0		0.01	
	$^{1}\Sigma_g^{+}$	0	3.8905	51				0.05	1
$^{24}\mathrm{Mg}^{35}\mathrm{Cl}$	$^{2}\Sigma^{+}$	0	2.2211	447	70	–3.54		3.14	
	$^{2}\Sigma^{+}$	0	2.1964	462				3.36	1,19,43
$^{24}\mathrm{Mg}^{35}\mathrm{Cl}^{-}$	$^{1}\Sigma^{+}$	0	2.4091	286	69	+3.54	1.57	1.20(Mg + Cl^{-})	
							1.59		19
$^{24}\mathrm{Mg}^{19}\mathrm{F}$	$^{2}\Sigma^{+}$	0	1.7659	706	72	–3.26		4.45	
	$^{2}\Sigma^{+}$	0	1.7500	720				4.75	1
$^{24}\mathrm{Mg}^{1}\mathrm{H}$	$^{2}\Sigma^{+}$	0	1.7400	1456	245	–1.37	7.11	1.36	
	$^{2}\Sigma^{+}$	0	1.7297	1495				1.34	1
$^{24}\mathrm{Mg}^{1}\mathrm{H}^{+}$	$^{1}\Sigma^{+}$	0	1.6546	1722	17	–3.51		1.97(Mg^{+} + H)	
	$^{1}\Sigma^{+}$	0	1.6519	1699				2.08	1
$^{24}\mathrm{Mg}^{1}\mathrm{H}^{-}$	$^{1}\Sigma^{+}$	0	1.8899	1070	1928	+1.74	0.81	1.26(Mg + H^{-})	
	$^{1}\Sigma^{+}$	0					1.05	1.53	27
$^{24}\mathrm{Mg}^{16}\mathrm{O}$	$^{1}\Sigma^{+}$	1089	1.7389	821	6	–7.19			
	$^{3}\Pi$	0	1.8882	626	42	–3.11		2.37	
	$^{3}\Pi$	2623	1.870	648					44
	$^{1}\Sigma^{+}$	0	1.7490	785				2.56 ± 0.2	1,44
$^{24}\mathrm{Mg}^{32}\mathrm{S}$	$^{1}\Sigma^{+}$	0	2.1492	528	6	–7.46		1.99	
	$^{1}\Sigma^{+}$	0	2.1425	529				2.39	1,19
$^{14}\mathrm{N}_2$	$^{1}\Sigma_g^{+}$	0	1.0902	2447	0	0	15.80	9.82	
	$^{1}\Sigma_g^{+}$	0	1.0977	2358			15.58	9.76	1
$^{14}\mathrm{N}_2^{+}$	$^{2}\Sigma_g^{+}$	0	1.1035	2330	0	0	29.18	8.66	
	$^{2}\Sigma_g^{+}$	0	1.1164	2207			27.1	8.71	1
$^{14}\mathrm{N}_2^{++}$	$^{1}\Sigma_g^{+}$	12281	1.1327	2077	0	0			
	$^{3}\Sigma_g^{-}$	2288	1.3517	1192	0	0			
	$^{3}\Pi_u$	0	1.2186	1654	0	0		–4.32(N^{+} + N^{+})	
	$^{3}\Sigma_g^{-}$	880		1460					45
	$^{1}\Sigma_g^{+}$	0	1.129	2008					45
$^{23}\mathrm{Na}_2$	$^{1}\Sigma_g^{+}$	0	3.0405	163	0	0	5.12	0.73	
	$^{1}\Sigma_g^{+}$	0	3.0789	159			4.90	0.72	1
$^{23}\mathrm{Na}_2^{+}$	$^{2}\Sigma_g^{+}$	0	3.5725	107	0	0		1.04	
	$^{2}\Sigma_g^{+}$	0						0.96	1
$^{23}\mathrm{Na}_2^{-}$	$^{2}\Sigma_u^{+}$	0	3.4723	99	0	0	0.46	0.64	
							0.43	(0.44)	1,19
$^{23}\mathrm{Na}^{35}\mathrm{Cl}$	$^{1}\Sigma^{+}$	0	2.3758	357	45	–8.75	9.07	3.97	
	$^{1}\Sigma^{+}$	0	2.3608	366		9.00	8.93	4.23 ± 0.1	1,19
$^{23}\mathrm{Na}^{35}\mathrm{Cl}^{+}$	$^{2}\Pi$	0	2.7970	157	32	–6.76		0.33(Na^{+} + Cl)	
								0.33	1
$^{23}\mathrm{Na}^{35}\mathrm{Cl}^{-}$	$^{2}\Sigma^{+}$	0	2.5158	263	44	+4.03	0.85	1.31(Na + Cl^{-})	
	$^{2}\Sigma^{+}$	0	2.497	265			0.73	1.34	40
$^{23}\mathrm{Na}^{19}\mathrm{F}$	$^{1}\Sigma^{+}$	0	1.9407	526	56	–8.00		4.71	

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Table 3 (*Continued*)

Molecule	State	T_e	r_e	ω_e	A	μ	E_i	D_0	Ref.(Exp.)
	$^{1}\Sigma^{+}$	0	1.9259	536		8.16		4.93	1
^{23}Na^{19}F^{-}	$^{2}\Sigma^{+}$	0	2.0150	438	62	+3.62	0.66	1.87(Na + F^{-})	
	$^{2}\Sigma^{+}$	0	2.005	430			0.52	2.12	40
^{23}Na^{1}H	$^{1}\Sigma^{+}$	0	1.8782	1161	203	–6.02		1.89	
	$^{1}\Sigma^{+}$	0	1.8865	1171		6.96		1.89	12,19,46
^{23}Na^{16}O	$^{2}\Sigma^{+}$	2434	1.9602	516	71	–7.87			
	$^{2}\Pi$	0	2.0634	482	35	–7.78	7.81	2.70	
	$^{2}\Sigma^{+}$	2050							47
	$^{2}\Pi$	0	2.0516	492				2.60	1,47
^{23}Na^{16}O^{+}	$^{3}\Pi$	2507	2.7700	77	23	–5.12			
	$^{3}\Sigma^{-}$	0	2.4983	195	18	–4.39		0.32(Na^{+} + O)	
								0.8	1
^{14}N^{35}Cl	$^{3}\Sigma^{-}$	0	1.6247	823	56	+1.15		2.95	
	$^{3}\Sigma^{-}$	0	1.6107	828				3.42 ± 0.1	19,48
^{20}Ne$_2$	$^{1}\Sigma_g^{+}$	0	(repulsive potential)						
	$^{1}\Sigma_g^{+}$	0	3.15 (r_0)	14 (ω_0)				0.002	1
^{20}Ne$_2$$^{+}$	$^{2}\Sigma_u^{+}$	0	1.8276	419	0	0		2.58	
	$^{2}\Sigma_u^{+}$	0						1.35	1
^{20}Ne^{40}Ar	$^{1}\Sigma^{+}$	0	(repulsive potential)						
	$^{1}\Sigma^{+}$	0	3.43					0.006 (D_e)	1
^{20}Ne^{1}H^{+}	$^{1}\Sigma^{+}$	0	1.0055	2780	823	+2.72		2.15(Ne + H^{+})	
	$^{1}\Sigma^{+}$	0		2900		3.00		2.08	1,22,23
^{14}N^{19}F	$^{3}\Sigma^{-}$	0	1.3173	1154	129	+0.14		3.58	
	$^{3}\Sigma^{-}$	0	1.3170	1141				3.52	1,19,48
^{14}N^{1}H	$^{3}\Sigma^{-}$	0	1.0393	3263	24	+1.54	13.65	3.60	
	$^{3}\Sigma^{-}$	0	1.0362	3282		1.39	≤13.49	≤ 3.47; 3.59	1,19
^{14}N^{1}H^{+}	$^{4}\Sigma^{-}$	1669	1.1135	2490	644	+1.53			
	$^{2}\Pi$	0	1.0778	2970	87	+1.73		3.63(N + H^{+})	
	$^{4}\Sigma^{-}$	509	1.0924	2673					49
	$^{2}\Pi$	0	1.0692	3048					49
^{14}N^{1}H^{-}	$^{2}\Pi$	0	1.0470	3065	490	+1.33	0.51	3.22(N + H^{-})	
	$^{2}\Pi$	0	1.040	3191			0.38	3.85	1,27,34
^{14}N^{16}O	$^{2}\Pi$	0	1.1445	1976	38	+0.12	9.68	6.62	
	$^{2}\Pi$	0	1.1508	1904	27–34	0.16	9.26	6.50	1
^{14}N^{16}O^{+}	$^{1}\Sigma^{+}$	0	1.0558	2481	28	–0.38	29.54	11.06(N + O^{+})	
	$^{1}\Sigma^{+}$	0	1.0632	2376			30.3	10.85	1
^{14}N^{16}O^{++}	$^{2}\Sigma^{+}$	0	1.0726	2265	4	–1.92		–3.83(N^{+} + O^{+})	
	($^{2}\Sigma^{+}$)	0							1
^{14}N^{16}O^{-}	$^{3}\Sigma^{-}$	0	1.2662	1435	53	+0.74	0.01	4.93(N + O^{-})	
	$^{3}\Sigma^{-}$	0	1.267	1470			0.02	5.06	1
^{14}N^{32}S	$^{2}\Pi$	0	1.4937	1254	9	+1.83	9.13	4.85	
	$^{2}\Pi$	0	1.4940	1219		1.81	8.87	4.77	1,19
^{14}N^{32}S^{+}	$^{1}\Sigma^{+}$	0	1.4282	1504	28	+2.12		6.27(N + S^{+})	
	$^{1}\Sigma^{+}$	0	1.440	1415				6.3	1
^{14}N^{32}S^{-}	$^{3}\Sigma^{-}$	0	1.6001	926	6	+1.45	1.25	3.90(N + S^{-})	
			1.589	880			1.19		19,34
^{16}O$_2$	$^{3}\Sigma_g^{-}$	0	1.2041	1636	0	0	12.52	5.28	
	$^{3}\Sigma_g^{-}$	0	1.2075	1580			12.07	5.12	1
^{16}O$_2$$^{+}$	$^{2}\Pi_g$	0	1.1054	2053	0	0	24.65	6.88	
	$^{2}\Pi_g$	0	1.1164	1905			24.2	6.66	1
^{16}O$_2$$^{++}$	$^{1}\Sigma_g^{+}$	0	1.0321	2420	0	0		–3.65(O^{+} + O^{+})	
	$^{1}\Sigma_g^{+}$	0							1
^{16}O$_2$$^{-}$	$^{2}\Pi_g$	0	1.3476	1178	0	0	0.19	3.77	
	$^{2}\Pi_g$	0	1.347	1089			0.44	4.09	1,34
^{16}O^{1}H	$^{2}\Pi$	0	0.9733	3704	11	+1.68	13.17	4.44	

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Table 3 (*Continued*)

Molecule	State	T_e	r_e	ω_e	A	μ	E_i	D_0	Ref.(Exp.)
	$^{2}\Pi$	0	0.9697	3738		1.67	13.01	4.39	1,30
$^{16}O^{1}H^{+}$	$^{3}\Sigma^-$	0	1.0372	3040	265	+2.03		4.94(O + H$^+$)	
	$^{3}\Sigma^-$	0	1.0289	3113		2.32		5.09	1,22
$^{16}O^{1}H^{-}$	$^{1}\Sigma^+$	0	0.9666	3668	195	+1.39	1.85	4.64(O$^-$ + H)	
	$^{1}\Sigma^+$	0	0.964	3738		1.04	1.83	4.76	1,22,34
$^{31}P_2$	$^{1}\Sigma_g^+$	0	1.8905	807	0	0	10.32	4.94	
	$^{1}\Sigma_g^+$	0	1.8934	781			10.53	5.03	1
$^{31}P_2^{+}$	$^{2}\Sigma_g^+$	3408	1.8881	768	0	0			
	$^{2}\Pi_u$	0	1.9787	701	0	0		5.01	
	$^{2}\Sigma_g^+$	(2179)	1.893	733 (ω_0)					1
	$^{2}\Pi_u$	0	1.9859	672				4.99	1
$^{31}P_2^{-}$	$^{2}\Pi_u$	0	1.9830	674	0	0	0.60	4.82	
	$^{2}\Pi$	0	1.979	640			0.59		3,34
$^{31}P^{35}Cl$	$^{3}\Sigma^-$	0	2.0393	528	64	–0.59		3.38	
	$^{3}\Sigma^-$	0	2.0146	551				2.96	19,50
$^{31}P^{19}F$	$^{3}\Sigma^-$	0	1.6062	830	120	–0.89	9.64	4.78	
	$^{3}\Sigma^-$	0	1.5897	847				4.51 ± 1.0	1,19
$^{31}P^{19}F^{+}$	$^{2}\Pi$	0	1.5182	1022	115	–2.61		5.52(P$^+$ + F)	
	$^{2}\Pi$	0	1.5003	1053					1
$^{31}P^{1}H$	$^{3}\Sigma^-$	0	1.4278	2338	76	+0.42	10.17	3.19	
	$^{3}\Sigma^-$	0	1.4214	2367			10.15	3.02	20,30,51
$^{31}P^{1}H^{+}$	$^{2}\Pi$	0	1.4331	2346	0	+0.64		3.41(P$^+$ + H)	
	$^{2}\Pi$	0	1.4352	2300 (ω_0)				≤3.36	1
$^{31}P^{1}H^{-}$	$^{2}\Pi$	0	1.4420	2213	296	+0.30	1.11	3.39(P + H$^-$)	
	$^{2}\Pi$	0	1.407	2230 (ω_0)			1.03	3.33	1,27
$^{31}P^{14}N$	$^{1}\Sigma^+$	0	1.4828	1406	1	–2.86	11.84	6.21	
	$^{1}\Sigma^+$	0	1.4909	1337		2.75	11.84	6.36 ± 0.2	1,19
$^{31}P^{14}N^{+}$	$^{2}\Sigma^+$	0	1.4756	1368	8	–2.05		4.75(P$^+$ + N)	
	$^{2}\Sigma^+$	0		(1200)				5.00	1
$^{31}P^{16}O$	$^{2}\Pi$	0	1.4801	1258	48	–2.06	8.56	6.13	
	$^{2}\Pi$	0	1.4764	1233		1.88	8.5	6.15	1,43,52
$^{31}P^{16}O^{+}$	$^{1}\Sigma^+$	0	1.4249	1455	17	–3.46		7.95(P$^+$ + O)	
	$^{1}\Sigma^+$	0	1.4250	1412				(8.4)	1,43
$^{31}P^{16}O^{-}$	$^{3}\Sigma^-$	0	1.5499	1032	77	–0.39	1.02	5.45(P + O$^-$)	
	$^{3}\Sigma^-$	0	1.540	1000 (ω_0)			1.09	5.78	1
$^{31}P^{32}S$	$^{2}\Pi$	0	1.9056	745	20	–0.68	8.06	4.44	
	$^{2}\Pi$	0	1.8977	739				4.54	1,53
$^{31}P^{32}S^{+}$	$^{1}\Sigma^+$	0	1.8282	866	15	–1.35		6.77(P$^+$ + S)	
	$^{1}\Sigma^+$	0		845					1
$^{32}S_2$	$^{3}\Sigma_g^-$	0	1.9070	715	0	0	9.55	4.39	
	$^{3}\Sigma_g^-$	0	1.8892	726			9.36	4.37	1
$^{32}S_2^{+}$	$^{2}\Pi_g$	0	1.8269	827	0	0		5.38	
	$^{2}\Pi_g$	0	1.825	790				5.37	1
$^{32}S_2^{-}$	$^{2}\Pi_g$	0	2.0284	564	0	0	1.57	3.94	
	$^{2}\Pi_g$	0		601			1.66	3.95	1
$^{32}S^{35}Cl$	$^{2}\Pi$	0	2.0000	558	22	–0.04		2.85	
	$^{2}\Pi$		1.975					2.83	19,43
$^{32}S^{19}F$	$^{2}\Pi$	0	1.6125	828	81	–0.85	10.20	3.64	
	$^{2}\Pi$	0	1.596	838		0.87	10.09	3.51	1,19,43
$^{32}S^{19}F^{+}$	$^{3}\Sigma^-$	0	1.5183	1001	82	–2.18		3.99(S$^+$ + F)	
									19
$^{32}S^{19}F^{-}$	$^{1}\Sigma^+$	0	1.7413	629	64	+0.77	2.13	2.90(S + F$^-$)	
							2.28		19
$^{32}S^{1}H$	$^{2}\Pi$	0	1.3471	2664	1	+0.80	10.46	3.65	
	$^{2}\Pi$	0	1.3409	2712		0.76	10.37	3.55	1,20,30

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Table 3 (*Continued*)

Molecule	State	T_e	r_e	ω_e	A	μ	E_i	D_0	Ref.(Exp.)
$\mathbf{^{32}S^{1}H^{+}}$	$^3\Sigma^-$	0	1.3714	2510	75	+1.10		3.74(S^+ + H)	
	$^3\Sigma^-$	0	1.3744 (r_0)					3.48	1
$\mathbf{^{32}S^{1}H^{-}}$	$^1\Sigma^+$	0	1.3485	2610	109	+0.60	2.34	3.79(S^- + H)	
	$^1\Sigma^+$	0	1.343	2647			2.32	3.79	1,34
$\mathbf{^{28}Si_2}$	$^3\Pi_u$	1215	2.1591	546	0	0			
	$^3\Sigma_g^-$	0	2.2678	500	0	0	7.87	3.19	
	$^3\Pi_u$		2.155	548					1
	$^3\Sigma_g^-$	0	2.246	511			7.92	3.21	1,54
$\mathbf{^{28}Si_2^{+}}$	$^4\Sigma_g^-$	0	2.2928	446	0	0		3.44	
									54
$\mathbf{^{28}Si_2^{-}}$	$^2\Sigma_g^+$	0	2.1055	589	0	0	1.87	3.87	
							2.20		19
$\mathbf{^{28}Si^{12}C}$	$^3\Sigma^-$	2471	1.8078	868	0	–2.58			
	$^3\Pi$	0	1.7138	982	17	–1.73	8.89	4.27	
	$^3\Sigma^-$	(5597)	(1.90)	(606)					1
	$^3\Pi$	0	1.722	965			9.0	(4.64)	1,55
$\mathbf{^{28}Si^{12}C^{+}}$	$^4\Sigma^-$	0	1.8257	812	29	–1.26		3.50(Si^+ + C)	
									55
$\mathbf{^{28}Si^{35}Cl}$	$^2\Pi$	0	2.0880	507	104	–0.96	7.40	4.30	
	$^2\Pi$	0	2.058	536			7.33	4.17	1,19,54,56
$\mathbf{^{28}Si^{35}Cl^{+}}$	$^1\Sigma^+$	0	1.9677	650	127	–3.35		5.02(Si^+ + Cl)	
									54
$\mathbf{^{28}Si^{35}Cl^{-}}$	$^3\Sigma^-$	0	2.2761	342	70	+2.17	1.19	1.98(Si + Cl^-)	
								1.40 ± 0.3	32
$\mathbf{^{28}Si^{19}F}$	$^2\Pi$	0	1.6196	833	127	–0.96	7.47	6.07	
	$^2\Pi$	0	1.6011	857			7.28	5.98	1,57
$\mathbf{^{28}Si^{19}F^{+}}$	$^1\Sigma^+$	0	1.5437	1016	131	–3.43		6.71(Si^+ + F)	
			1.527						1,32
$\mathbf{^{28}Si^{19}F^{-}}$	$^3\Sigma^-$	0	1.7058	651	97	+1.95	0.72	3.23(Si + F^-)	
							1.34 ± 0.3		32
$\mathbf{^{28}Si^{1}H}$	$^2\Pi$	0	1.5275	2013	280	+0.07	8.01	3.12	
	$^2\Pi$	0	1.5197	2042			≤8.04	≤3.06	1,43
$\mathbf{^{28}Si^{1}H^{+}}$	$^1\Sigma^+$	0	1.5144	2126	76	+0.17		3.22(Si^+ + H)	
	$^1\Sigma^+$	0	1.5041	2157				3.17	1
$\mathbf{^{28}Si^{1}H^{-}}$	$^3\Sigma^-$	0	1.5573	1816	559	+0.13	1.28	3.05(Si^- + H)	
	$^3\Sigma^-$	0	1.5658	1804			1.28	≤2.95	1,27
$\mathbf{^{28}Si^{14}N}$	$^2\Pi$	849	1.6400	1063	17	–2.81			
	$^2\Sigma^+$	0	1.5674	1183	25	–2.78		4.61	
	$^2\Pi$	2032	1.642	1032					
	$^2\Sigma^+$	0	1.5719	1151				4.68	1,58
$\mathbf{^{28}Si^{16}O}$	$^1\Sigma^+$	0	1.5131	1258	50	–3.13	11.45	8.04	
	$^1\Sigma^+$	0	1.5097	1242		3.10	11.49	8.26	1,19
$\mathbf{^{28}Si^{16}O^{+}}$	$^2\Sigma^+$	0	1.5233	1143	2	–4.39		4.71(Si^+ + O)	
	$^2\Sigma^+$	0	1.5191 (r_0)					4.98	1
$\mathbf{^{28}Si^{31}P}$	$^2\Sigma^+$	0	1.9829	686	3	–1.47		3.54	
								3.73	1
$\mathbf{^{28}Si^{32}S}$	$^1\Sigma^+$	0	1.9392	744	51	–1.81		6.09	
	$^1\Sigma^+$	0	1.9293	750		–1.73		6.42	1
$\mathbf{^{32}S^{16}O}$	$^3\Sigma^-$	0	1.4919	1152	15	–1.56	10.54	5.36	
	$^3\Sigma^-$	0	1.4811	1149		–1.55	10.29	5.36	1
$\mathbf{^{32}S^{16}O^{+}}$	$^2\Pi$	0	1.4240	1368	5	–2.29		5.37(S^+ + O)	
	$^2\Pi$	0	1.424	1360				5.43	1
$\mathbf{^{32}S^{16}O^{-}}$	$^2\Pi$	0	1.5901	888	26	–0.72	0.96	4.31(S^- + O)	
							1.13		3

7. ISOTROPIC HYPERFINE COUPLING CONSTANTS OF POLYATOMIC MOLECULES

For this sensitive property, the contractions of the cc-pvqz basis sets were completely resolved.

For some diatomic molecules (Cl_2^-, ClF^-, F_2^-) the calculations were performed at the calculated bond length (above) and the still uncertain experimental bond length (below in parentheses). Tables for calculated or experimental hfc constants are rare in review articles. Table 4 represents, to our knowledge, the largest set of hfc constants where 20 molecules were investigated to compare the hfc constants of 34 nuclei with experimental data. Irrespective of the meaning of the overall statistics, the mean absolute deviation $\overline{|\Delta A_{iso}|}$ resulted to be 10.1 G for an absolute range of A_{iso} of 406 G. There are only two nuclei, Al in AlO and F in ClF^-, for which the calculated values deviate markedly (~100 G) from the experiment. When these two nuclei are removed from the statistics, the mean absolute deviation for A_{iso} is reduced to 3.6 G. In particular, the nuclei H, B, C, N, and O exhibit good agreement between the calculated and experimental hfc constants.

Table 4 Calculated and experimental isotropic hyperfine coupling constants A_{iso} / G.

Radical	State	Nucleus		A_{iso}(calc.)	A_{iso}(exp.)	Ref.(Exp.)
AlO	$^2\Sigma^+$	^{27}Al		163.7	273 (Ne)	59
					321 (Ar)	
					328 (Kr)	
BS	$^2\Sigma^+$	^{11}B		291.5	284 (Ne)	60
					292 (Ar)	
CH	$^2\Pi$	^{13}C		19.1	16.8	61
		^{1}H		–16.0	–20.6	
			r(ClCl)			
Cl_2^-	$^2\Sigma_u^+$	^{35}Cl	2.717	25.9		
			(2.63)[a]	31.0	38.9	62
			r(ClF)			
ClF^-	$^2\Sigma^+$	^{35}Cl	2.284	32.3		
			(2.09)[a]	49.3	54.3	62
		^{19}F	2.284	212.8		
			(2.09)[a]	325.8	209.3	
CN	$^2\Sigma^+$	^{13}C		205.2	209.8	62
		^{14}N		–6.7	–4.5	
			r(FF)			
F_2^-	$^2\Sigma_u^+$	^{19}F	2.019	202.3		
			(1.89)[a]	270.5	280.2 (NaF)	62
					267.9 (Ne)	
NO	$^2\Pi$	^{14}N		6.4	7.9	63
		^{17}O		–9.6	–	
OH	$^2\Pi$	^{17}O		–15.3	–18.3	62
		^{1}H		–22.3	–22.8	

(*Continued on next page*)

Table 4 (*Continued*)

Radical	State	Nucleus	A_{iso}(calc.)	A_{iso}(exp.)	Ref.(Exp.)
				–26.2	
SH	$^2\Pi$	^1H	–13.6	–23.2	64
BO	$^2\Sigma^+$	^{11}B	381.3	365.7	65
O_2	$^3\Sigma_g^-$	^{17}O	–13.9	–19.6	66
CH_3	$^2A_2''$	^{13}C	29.2	27	67
		^1H	–21.8	–25	
NH_2	$^2B_1$	^{14}N	9.9	9.96	63
		^1H	–20.4	–24.0	
H_2O^+	$^2B_1$	^{17}O	–23.2	–29.7	68
		^1H	–23.7	–26.1	
C_2H	$^2\Sigma^+$	^{13}C	375.6	362	67
		$^{13}C(H)$	80.7	76	
		^1H	18.8	18	
H_2CN	$^2B_1$	^{13}C	–24.4	–29	69
		^{14}N	8.1	9	
		^1H	81.3	83	
C_2O	$^3\Sigma^-$	^{13}C	14.2	11.4	70
		$^{13}C(O)$	–6.9	–10.0	
C_3H_5(Allyl)	$^2A_2$	^{13}C (CH_2)	18.6	21.9	67
		^{13}C	–16.0	–17.2	
		^1H (trans HCCC)	–14.4	–14.8	
		^1H (cis HCCC)	–13.5	–13.9	
		^1H (CH)	4.2	4.2	
$C_6H_5CH_2$	$^2B_1$	^{13}C (CH_2)	20.9		
		^{13}C	–13.7		
		^{13}C (o)	7.9		
		^{13}C (m)	–7.0		
		^{13}C (p)	8.3		
		^1H (CH_2)	–15.75	–16.35	71
		^1H (o)	–5.24	–5.14	
		^1H (m)	2.22	1.75	
		^1H (p)	–6.15	–6.14	

[a] Uncertain experimental bond length

8. STRUCTURES OF POLYATOMIC GAS-PHASE MOLECULES

Experimentally obtained molecular structures (MW, ED) can be as uncertain as calculated structures. Even for the seemingly well-understood methane molecule CH_4, the spectroscopically estimated CH distance had to be corrected repeatedly over the years: 1966: 1.0940 Å [72], 1985: 1.092 Å [12], 1994: 1.086 ± 0.002 Å [73], and 1999: 1.0870 Å [19]. For the ammonia–borane molecule NH_3BH_3 only two different values r(BN) = 1.56 and 1.60 Å from X-ray diffraction studies of the crystal structure [74] were available over almost 30 years for comparison with calculated structures [12]. In 1983, microwave spectroscopy suggested r(BN) = 1.6576 Å [75] in excellent agreement with calculated structures. In Table 5, the calculated geometries of 53 polyatomic molecules are compared with experimental data; 74 out of a set of 109 calculated bond lengths differ by the order of 10^{-3} Å or less from experimental values.

The worst cases are those compounds where sulfur and/or chlorine are involved. The calculated SF bond length in NSF is too long by 0.033 Å, compared with the experimental structure [12]; the calculated SCl bond length in SCl_2 is too long by 0.037 Å, compared with the experimental structure [19]; and that in $OSCl_2$ turned out to be too long by 0.048 Å, compared with the experimental structure [19]. The calculated ClO bond length in dichlorine peroxide ClO_2Cl resulted to be too long by 0.052 Å, compared with the structure from microwave analysis [76]. For more details, see Section 11.

The C_5O molecule is an example where two arguments favor the calculated structure, but not that from the recent microwave analysis [77]. At first, the sequence of the CC distances should be in accordance with the commonly accepted polyacetylene structure $^{+}$:O≡C1–C2≡C3–C4≡C5:$^{-}$; and second, the calculated rotational constant (1369 MHz) is in almost perfect agreement with the observed one (1367 MHz).

Another example where an experimental bond length is rebutted in the literature is NH_3BF_3. Similar to NH_3BH_3, the BN bond length in NH_3BF_3 is likely 0.06–0.10 Å larger than the hitherto assumed value of r(BN) = 1.59 Å [12,78] in agreement with calculated values.

A difficult geometry parameter is the SO_H bond length in the sulfuric acid molecule H_2SO_4. Calculated values from the literature overestimate that from microwave spectroscopy by 0.048 Å. B3LYP density functional theory in conjunction with extended basis sets (cc-pvqz) reduces this discrepancy to 0.026 Å (cf. Table 5).

Table 5 Calculated and experimental equilibrium geometries (interatomic distances r / Å and angles < / degrees) for selected polyatomic gas–phase molecules.

Molecule	Point Group	Geometrical Parameter	Calc.	Exp.	Ref.(Exp.)
CH_4	T_d	r(CH)	1.0876	1.0870	19
NH_3	C_{3v}	r(NH)	1.0126	1.012	12
		<(HNH)	106.8	106.7	
H_2O	C_{2v}	r(OH)	0.9603	0.9575	19
		<(HOH)	104.9	104.51	
SiH_4	T_d	r(SiH)	1.4788	1.4798	19
PH_3	C_{3v}	r(PH)	1.4182	1.4200	19
		<(HPH)	93.5	93.345	
H_2S	C_{2v}	r(SH)	1.3426	1.3356	19
		<(HSH)	92.5	92.12	
C_2H_2	$D_{\infty h}$	r(CC)	1.1952	1.203	19

(*Continued on next page*)

Table 5 (*Continued*)

Molecule	Point Group	Geometrical Parameter	Calc.	Exp.	Ref.(Exp.)
		r(CH)	1.0608	1.060	
C_2H_4	D_{2h}	r(CC)	1.3240	1.339	19
		r(CH)	1.0819	1.087	
		<(HCH)	116.5	117.4	
C_2H_6	D_{3d}	r(CC)	1.5269	1.5351	19
		r(CH)	1.0904	1.0940	
		<(HCH)	107.5	107.8	
HCN	$C_{\infty v}$	r(CN)	1.1450	1.1532	19
		r(CH)	1.0654	1.0655	
HCP	$C_{\infty v}$	r(CP)	1.5338	1.5398	19
		r(CH)	1.0700	1.0692	
CH_3OH	C_s	r(CO)	1.4201	1.4246	12,19
		$r(\mathrm{CH_{tr}})$	1.0878	1.0936 (av.)	
		$r(\mathrm{CH_g})$	1.0939	"	
		r(OH)	0.9594	0.9451	
		<$(\mathrm{OCH_{tr}})$	106.9	107.2	
		<$(\mathrm{OCH_{g,g'}})$[a]	130.6	129.9	
		<$(\mathrm{H_gCH_{g'}})$	108.9	108.63	
		<(COH)	108.9	108.53	
CH_3SH	C_s	r(CS)	1.8261	1.819	12
		$r(\mathrm{CH_{tr}})$	1.0870	1.091	
		$r(\mathrm{CH_g})$	1.0862	1.091	
		r(SH)	1.3429	1.336	
		<$(\mathrm{SCH_{tr}})$	106.1	–	
		<$(\mathrm{SCH_{g,g'}})$[a]	129.5	–	
		<$(\mathrm{H_gCH_{g'}})$	110.4	109.8	
		<(CSH)	97.3	96.5	
CH_3F	C_{3v}	r(CF)	1.3883	1.382	19
		r(CH)	1.0892	1.095	
		<(HCH)	110.0	110.45	
NH_3BH_3	C_{3v}	r(BN)	1.6563	1.6576	75
		r(BH)	1.2063	1.2160	
		r(NH)	1.0143	1.0140	
		<(HBH)	113.5	113.8	
		<(HNH)	107.9	108.6	
NH_2OH	C_s trans	r(NO)	1.4426	1.453	12
		r(NH)	1.0155	1.016	
		r(OH)	0.9603	0.962	
		<$(\mathrm{ONH_{a,a'}})$[a]	113.8	112.6	
		<(HNH)	105.9	107.1	

(*Continued on next page*)

Table 5 (*Continued*)

Molecule	Point Group	Geometrical Parameter	Calc.	Exp.	Ref.(Exp.)
		<(NOH)	102.7	101.4	
H_2O_2	C_2	*r*(OO)	1.4490	1.452	12,79
		r(OH)	0.9652	0.965	
		<(HOO)	100.7	100.0	
		<(HOOH)	113.1	111.5	
H_2CO	C_{2v}	*r*(CO)	1.1981	1.208	12
		r(CH)	1.1057	1.116	
		<(HCH)	116.0	116.5	
HOF	C_s	*r*(OF)	1.4288	1.442	12
		r(OH)	0.9696	0.966	
		<(HOF)	98.6	96.8	
H_2CCCH_2	D_{2d}	*r*(CC)	1.2995	1.3084	19
		r(CH)	1.0826	1.087	
		<(HCH)	117.4	118.2	
H_2CN_2	C_{2v}	*r*(NN)	1.1311	1.12	19
		r(CN)	1.2908	1.32	
		r(CH)	1.0750	1.075	
		<(HCH)	124.1	126.0	
CO_2	$D_{\infty h}$	*r*(CO)	1.1588	1.1600	19
OCS	$C_{\infty v}$	*r*(CO)	1.1542	1.1578	19
		r(CS)	1.5641	1.5601	
CS_2	$D_{\infty h}$	*r*(CS)	1.5544	1.5526	19
NSF	C_s	*r*(NS)	1.4416	1.448	12
		r(SF)	1.6761	1.643	
		<(NSF)	116.3	116.9	
O_3	C_{2v}	*r*(OO)	1.2532	1.2716	19
		<(OOO)	118.2	117.47	
SO_2	C_{2v}	*r*(SO)	1.4419	1.4308	19
		<(OSO)	118.6	119.329	
$SiCl_2$	C_{2v}	*r*(SiCl)	2.0977	2.0653	80
		<(ClSiCl)	101.8	101.324	
SCl_2	C_{2v}	*r*(SCl)	2.0428	2.006	19
		<(ClSCl)	104.0	103.0	
OClO	C_{2v}	*r*(ClO)	1.478	1.470	19
		<(OClO)	117.3	117.38	

(*Continued on next page*)

Table 5 (*Continued*)

Molecule	Point Group	Geometrical Parameter	Calc.	Exp.	Ref.(Exp.)
HNO_2	C_s	r(NO)	1.1627	1.170	19
	trans	r(NO_H)	1.4297	1.432	
		r(OH)	0.9669	0.958	
		<(ONO)	111.1	110.7	
		<(NOH)	102.7	102.1	
HNO_3	C_s	r(NO_{cis})	1.2066	1.21	19
	planar	r(NO_{tr})	1.1913	1.20	
		r(NO_H)	1.4097	1.41	
		r(OH)	0.9701	0.96	
		<($O_{cis}NO_H$)	115.6	115.9	
		<($O_{tr}NO_H$)	114.0	113.9	
		<(NOH)	103.1	102.2	
FN_3	C_s	r(FN1)	1.4248	1.444	81
	trans	r(N1N2)	1.2513	1.253	
		r(N2N3)	1.1267	1.132	
		<(N1N2N3)	171.8	170.9	
		<(FN1N2)	105.3	103.8	
N_2F_2	C_{2h}	r(NN)	1.2146	1.214	12
	trans	r(NF)	1.3844	1.384	
		<(NNF)	105.7	114.5	
ClN_3	C_s	r(ClN1)	1.7610	1.745	81
	trans	r(N1N2)	1.2420	1.252	
		r(N2N3)	1.1265	1.133	
		<(N1N2N3)	172.1	171.9	
		<(ClN1N2)	110.1	108.6	
C_4H_6	C_{2h}	r(C1C2)	1.3336	1.349	19
		r(C2C3)	1.4526	1.467	
		r(C1H)	1.0802	1.08 (av.)	
		r(C1H')	1.0826	"	
		r(C2H)	1.0852	"	
		<(C1C2C3)	124.3	124.4	
		<(HC1C2)	121.7	120.9 (av.)	
		<(H'C1C2)	121.4	"	
		<(HC2C1)	119.3	"	
C_3O	$C_{\infty v}$	r(C1O)	1.1488	1.150	82
		r(C1C2)	1.2942	1.306	
		r(C2C3)	1.2670	1.254	
C_5O	$C_{\infty v}$	r(C1O)	1.1555	1.1562	77
		r(C1C2)	1.2828	1.2552	
		r(C2C3)	1.2592	1.2881	
		r(C3C4)	1.2897	1.2947	

(*Continued on next page*)

Table 5 (*Continued*)

Molecule	Point Group	Geometrical Parameter	Calc.	Exp.	Ref.(Exp.)
		r(C4C5)	1.2744	1.2736	
OC_3O	$D_{\infty h}$	*r*(CO)	1.1597	1.1632	83
		r(CC)	1.2715	1.2894	
C_2S	$C_{\infty v}$	*r*(CS)	1.5712	1.567	84
		r(CC)	1.3094	1.310	
C_3S	$C_{\infty v}$	*r*(C1S)	1.5426	1.5323	85
		r(C1C2)	1.2892	1.3028	
		r(C2C3)	1.2749	1.2724	
SC_3S	$D_{\infty h}$	*r*(CS)	1.5595	1.56	86
		r(CC)	1.2728	1.28	
ClO_2Cl	C_2	*r*(OO)	1.3593	1.4259	76
		r(OCl)	1.7559	1.7044	
		<(ClOO)	111.5	110.07	
		<(ClOOCl)	84.9	81.03	
NO_3^-	D_{3h}	*r*(NO)	1.2558	1.22 – 1.27	12
BF_3	D_{3h}	*r*(BF)	1.3134	1.313	19
NF_3	C_{3v}	*r*(NF)	1.3774	1.365	12
		<(FNF)	102.0	102.5	
PF_3	C_{3v}	*r*(PF)	1.5831	1.570	19
		<(FPF)	97.6	97.8	
P_4	T_d	*r*(PP)	2.2077	2.21	19
NH_3BF_3	C_{3v}	*r*(BN)	1.6943	1.59 (?)[b]	12,78
		r(BF)	1.3703	1.38	
		r(NH)	1.0148	–	
		<(FBF)	114.3	111.0	
		<(HNH)	108.7	–	
H_2SO_4	C_2	*r*(SO)	1.4257	1.422	19
		r(SO_H)	1.5997	1.574	
		r(OH)	0.9674	0.97	
		<(OSO)	124.0	123.3	
		<(O_HSO_H)	102.0	101.3	
		<(HOS)	109.0	108.5	
		<($OOSO_H$)	–125.1		
		<(OSO_HH)	–29.7	–20.8	
ONF_3	C_{3v}	*r*(NO)	1.1516	1.158	86
		r(NF)	1.4385	1.431	

(*Continued on next page*)

Table 5 (*Continued*)

Molecule	Point Group	Geometrical Parameter	Calc.	Exp.	Ref.(Exp.)
		<(FNF)	100.5	100.8	
$OSCl_2$	C_s	r(SO)	1.4418	1.44	19
		r(SCl)	2.1202	2.072	
		<(OSCl)	107.8	108.0	
		<(ClSCl)	98.2	97.2	
SF_6	O_h	r(SF)	1.5827	1.561	19

[a] The notation $<(ABH_{d,e})$ is used to describe the angle between the AB bond and the H_dBH_e plane.
[b] Question–marks are taken from the literature.

9. ANHARMONICITIES OF DIATOMIC MOLECULES

For the calculation of anharmonicities, the potential energy curves were represented by means of a point grid of 0.1 a_0 and roughly 25 points. These were interpolated by a polynomial fit from which the anharmonicities $\omega_e x_e$ within the framework of a Dunham analysis were derived. All experimental values are taken from ref. 1. The comparison of calculated and experimental values in Table 6 indicates a remarkably strong relation between anharmonicities and reduced masses of the vibrating systems and a surprisingly good agreement. Anharmonicities are useful for deriving ω_0 values according to $\omega_0 = \omega_e - 2\omega_e x_e$. The statistics of deviations between calculated and experimental anharmonicities can be found in Table 2.

Table 6 Calculated and experimental anharmonicities $\omega_e x_e$ / cm^{-1}.

Molecule	$\omega_e x_e$(calc.)	$\omega_e x_e$(exp.)
$^{27}Al^{1}H$	27	29.09
$^{9}Be^{1}H$	35	36.31
$^{9}Be^{1}H^{+}$	35	39.79
$^{9}Be^{16}O$	11	11.83
$^{11}B^{19}F$	12	11.84
$^{11}B^{1}H$	47	49.39
$^{11}B^{16}O$	11	11.81
$^{12}C^{19}F$	11	11.10
$^{12}C^{1}H$	59	63.02
$^{12}C^{14}N$	13	13.09
$^{12}C^{14}N^{+}$	15	16.14
$^{12}C^{16}O$	13	13.29
$^{1}H_2$	115	121.34
$^{1}H^{35}Cl$	50	52.82
$^{4}He^{1}H^{+}$	153	157.7
$^{1}H^{19}F$	87	89.88
$^{7}Li^{1}H$	21	23.20
$^{24}Mg^{1}H$	32	31.89
$^{24}Mg^{1}H^{+}$	29	31.93
$^{14}N_2$	13	14.32
$^{14}N_2^{+}$	14	16.10
$^{23}Na^{1}H$	16	19.72

(*Continued on next page*)

Table 6 (*Continued*)

Molecule	$\omega_e x_e$(calc.)	$\omega_e x_e$(exp.)
$^{14}N^1H$	71	78.35
$^{14}N^{16}O$	13	14.07
$^{14}N^{16}O^+$	14	16.26
$^{16}O_2$	10	11.98
$^{16}O_2^+$	13	16.26
$^{16}O^1H$	78	84.88
$^{16}O^1H^+$	81	78.52
$^{31}P^1H$	39	44.5
$^{28}Si^1H$	34	35.51
$^{32}S^1H$	45	(59.9)

10. NMR CHEMICAL SHIFTS OF POLYATOMIC MOLECULES

The calculation of NMR chemical shifts is confronted with "easy" and "difficult" (quadrupole effects) nuclei as well as with "normal" and "unusual" (diradicaloid character) bonding situations. Experience has shown that computational procedures such as GIAO (gauge-independent atomic orbitals) have much success where ^1H and ^{13}C nuclei are involved in the molecules (Tables 7a, 7b). Calculated chemical shifts of the nuclei ^{15}N, ^{17}O, and ^{19}F are also in good agreement with experimental values for many compounds. However, there are exceptional molecules where all attempts of calculations fail dramatically. The same is true for ^{29}Si, ^{31}P, ^{33}S, and ^{35}Cl. Worst cases are defined here by discrepancies of the size

Table 7a Relative shifts $\delta(^1H)$ referenced to TMS; CH_4 was used as primary reference for the calculated data, a value of $\delta(CH_4) = 0.1$ ppm was used for conversion, the calculated shielding $\sigma(^1H)$ of CH_4 is 31.5 ppm. Experimental values are for gas-phase molecules unless otherwise stated.

		$\delta(^1H)$(calc.)	$\delta(^1H)$(exp.)
CH_4		0.1	0.1
H_2O		0.5	0.7
NH_3		–0.2	0.1
HF		2.3	2.6
PH_3		1.9	1.6
SiH_4		3.5	3.1
H_2S		0.8	0.2
HCl		0.5	–0.3
C_2H_2		1.0	1.5
C_2H_4		5.6	5.3
C_2H_6		0.8	0.9
HCN		2.3	2.8
CH_3OH	H(C)	3.5	3.4
	H(O)	–0.4	0.0
CH_3F		4.3	4.1
HOF		11.8	12.0
CH_3SH	H(C)	2.0	1.2 (liq.)
	H(S)	1.5	2.1 (liq.)

$$|\delta(\text{calc.}) - \delta(\text{exp.})| = |\Delta\delta| > 100 \text{ ppm and } 100\%|\Delta\delta|/|\delta(\text{exp.})| > 10\%.$$

All references for experimental NMR chemical shifts in the Tables 7a–h can be found in ref. 87. The relation between absolute shieldings σ and relative shifts δ is $\delta = \sigma_{ref} - \sigma$ where all data are given in ppm. All reported relative NMR chemical shifts δ are isotropic shifts, $\delta_{iso} = 1/3(\delta_{xx} + \delta_{yy} + \delta_{zz})$.

The calculated relative shift σ (^{15}N) = 1017 ppm in the NSF molecule differs by 752 ppm (284%) from the experimental value of 265 ppm, according to IGLO(II) *ab initio* RHF calculations from the literature. Recent GIAO/B3LYP/cc-pvqz calculations (Table 7c) reduce this error from 752 (284%) to 455 ppm (172%). Difficult molecules for the calculation of relative shifts δ (^{17}O) are O_3, but also SO_2 and $OSCl_2$ (Table 7d). Different attempts at calculations for O_3 are summarized in Table 7h. *Ab initio* RHF calculations for O_3 fail by ~10^3 ppm. Such errors were attributed to the lack of electron correlation in

Table 7b Relative shifts $\delta(^{13}C)$ referenced to TMS; CH_4 was used as primary reference for the calculated data, a value of $\delta(CH_4)$ = –7.0 ppm was used for conversion, the calculated shielding $\sigma(^{13}C)$ of CH_4 is 189.0 ppm. Experimental values are for gas-phase molecules unless otherwise stated.

		$\delta(^{13}C)$(calc.)	$\delta(^{13}C)$(exp.)
CH_4		–7.0	–7.0
HCN		109.7	106.0
CH_3OH		55.2	51.5
CH_3F		75.6	71.3
C_2H_2		73.0	70.9
C_2H_4		131.4	123.6
C_2H_6		9.1	7.2
CO_2		131.5	129.3
CS_2		212.8	196.1
CO		197.4	187.1
OCS		164.1	158.1
$CFCl_3$		157.8	117.6 (liq.)
$(CH_3)_3C^+$	C^+	356.8	335.7 (liq.)
	CH_3	51.6	48.3 (liq.)
H_2CCCH_2	C	229.4	214
	CH_2	75.8	78
CH_3SH		12.3	6.5 (liq.)

Table 7c Relative shifts $\delta(^{15}N)$ referenced to NH_3; the calculated shielding $\sigma(^{15}N)$ of NH_3 is 262.5 ppm. Experimental values are for liquid-phase molecules unless otherwise stated.

		$\delta(^{15}N)$(calc.)	$\delta(^{15}N)$(exp.)
NH_3		0.0	0.0
HCN		306.0	290.5 (gas)
N_2		346.6	364.5 (gas)
NP		681.4	612.5 (gas)
NSF		720.5	264.7
NF_3		437.4	371
N_2F_2	trans	506.7	446
H_2CN_2	N(C)	314.0	286
	N	441.3	397

Table 7d Relative shifts $\delta(^{17}O)$ referenced to H_2O (liq.); H_2O (gas) was used as primary reference for the calculated data, a value of $\delta(H_2O) = -36.1$ ppm was used for conversion, the calculated shielding $\sigma(^{17}O)$ of H_2O is 329.8 ppm.

		$\delta(^{17}O)$(calc.)	$\delta(^{17}O)$(exp.)
H_2O		–36.1	–36.1 (gas)
H_3O^+		–10.3	9.1 (liq.)
CH_3OH		–30.8	–38
CO		368.1	350 (gas)
CO_2		78.5	64.5 (gas)
COS		218.2	200 (gas)
NO_3^-		437.3	410 (liq.)
$OSCl_2$ (C_s)		374.6	292 (liq.)
H_2O_2		189.0	174 (liq.)
O_3	O (cent.)	1375.5	1032
	O (term.)	1835.2	1598
SO_2		612.7	513 (liq.)

Table 7e Relative shifts $\delta(^{19}F)$ referenced to $CFCl_3$; the calculated shielding $\sigma(^{19}F)$ of $CFCl_3$ is 162.1 ppm. Experimental values are for gas-phase molecules unless otherwise stated.

		$\delta(^{19}F)$(calc.)	$\delta(^{19}F)$(exp.)
$CFCl_3$		0.0	0.0
HF		–247.6	–214.4
BF_3		–143.3	–131.6
F_2		359.6	428.4
CH_3F		–300.9	–275.4
ClF		–501.1	–441.5
SF_6		78.4	56.1
NF_3		139.2	145.3
PF_3		–40.1	–32.7
NSF		273.7	234 (liq.)
N_2F_2	trans	96.6	90 (liq.)

Table 7f Relative shifts $\delta(^{31}P)$ referenced to 85 % H_3PO_4; PH_3 was used as primary reference for the calculated data, a value of $\delta(PH_3) = -240$ ppm was used for conversion, the calculated shielding $\sigma(^{31}P)$ of PH_3 is 586.3 ppm.

	$\delta(^{31}P)$(calc.)	$\delta(^{31}P)$(exp.)
PH_3	–240	–240
PH_4^+	–97.8	–101
PN	325.1	302
FCP	–321.2	–207
HCP	–9.0	–32
PF_3	120.4	97
P_4	–505.5	–553 (sol.)

Table 7g Relative shifts $\delta(^{33}S)$ referenced to CS_2; the calculated shielding $\sigma(^{33}S)$ of CS_2 is 526.4 ppm.

	$\delta(^{33}S)$(calc.)	$\delta(^{33}S)$(exp.)
CS_2	0.0	0.0
H_2S	–188.4	–171.0
CH_3SH	–103.8	–125
COS	–257.9	–261.8
SO_2	748.8	706.9
$OSCl_2$ (C_s)	638.8	556
SF_6	212.8	155.4 (gas)

Table 7h Several attempts for the calculation of $\delta(^{17}O)$ relative shifts of the ozone molecule, O1–O2–O.

Method	$\delta(^{17}O1)$	$\delta(^{17}O2)$
RHF/IGLO(II)	3321	3216
RHF/GIAO/6–311+G(2d)	3624	3513
MP2/GIAO/6–311+G(2d)	–2084	–4246
B3LYP/GIAO/cc–pvqz	1835	1375
Exp.	1598	1032

the RHF wave functions. Therefore, *ab initio* MP2/6-311+G(2d) calculations were performed. However, entirely wrong results were obtained for O_3. Finally, GIAO/B3LYP/cc-pvqz calculations yielded qualitatively correct results for O_3, but the deviations from experimental data are still unusually high (200–300 ppm). A further source for remarkable deviations of δ (^{17}O) data can be seen in the values from the liquid phase, for example, SO_2 and H_3O^+. A difficult phosphorus-containing molecule is FCP, where RHF *ab initio* as well as DFT calculations fail by more than 100 ppm for the relative shift δ (^{31}P).

Statistics for the deviations between calculated and experimental NMR chemical shifts δ are meaningful only under special conditions: 1) The number N of investigated systems should be as large as possible. 2) The mean absolute deviation $\overline{|\Delta\delta|}$ should be seen only in connection with the width of the global range of δ. 3) The breakdown of the calculation for some examples makes any statistics for the respective nucleus meaningless.

The mean absolute deviation for δ (^{1}H) values in Table 7a is as low as 0.4 ppm, but the range of δ (^{1}H) is also very low (12.3 ppm). The mean absolute deviation for δ (^{13}C) values in Table 7b is 9.2 ppm, where the range of δ (^{13}C) is 342.7 ppm. For ^{15}N in Table 7c, the disaster with the NSF molecule makes statistics meaningless. Statistics from the literature where NSF is not included are, therefore, misleading [17]. In addition, cations and anions are excluded from these statistics so that the respective δ ranges and, consequently, the mean absolute deviations are low, simulating best agreement between calculations and experiments. A similar situation can be found in Table 7d for ^{17}O, where the O_3 molecule destroys any usefulness of statistics (cf. also Table 7h). For the nuclei ^{19}F, ^{31}P, and ^{33}S, the mean absolute deviations and, in parentheses, the widths of the δ ranges are (in ppm) 28.1 (869.9), 39.1 (855), and 37.3 (968.7), respectively. For example, the global δ range of ^{31}P for *all* presently known phosphorus compounds is as large as 2000 ppm. The utility of calculated NMR chemical shifts is restricted mainly to the description of trends of related compounds.

11. CONCLUDING REMARKS ON CALCULATED VERSUS EXPERIMENTAL PROPERTIES AND COMPUTATIONALLY DEMANDING MOLECULES

The meaning of this project can be demonstrated best by means of the pair of SiF and SiCl radicals. The four steps in chronological order in Table 8 are as follows: 1) The experimental dissociation energies were originally found in well-established tables [1,2]. 2) During the preparation of this project these radicals turned out to be bad D_0 systems in the sense of large discrepancies (~ 0.5 eV) between experimental and B3LYP calculated D_0 values. 3) Members from the family of bad D_0 systems were selected for accurate time-consuming *ab initio* CCSD(T) calculations. As a result, these calculations favor the B3LYP calculated D_0 values over the experimental ones [88]. 4) Additional experimental D_0 data were found which are in excellent agreement with the B3LYP calculated values of this project. However, for SiF, these are not yet included in well-known tables such as [19] so that primary references [57] were late in finding, and for SiCl, these have been included in well-known tables [56] very recently, but primary references were not found.

The noble gas compound He_2^+ exhibits large deviations between B3LYP calculated and accurate experimental properties. *Ab initio* CCSD(T) calculations confirm in this case the complete breakdown of the B3LYP procedure in its present form. Fortunately, He_2^+ is unique in this respect. This is an important result from this study of a large number of molecules.

The bond length of the anion Cl_2^- is considered not to be well established from the experimental point of view. The B3LYP calculated bond length differs markedly from the experimentally estimated value. Recently performed CCSD(T) calculations did not solve the problem. Instead, a third quite dif-

Table 8 Properties of selected diatomic molecules in their chronological order.

Molecule		r_e / Å	ω_e / cm^{-1}	D_0 / eV	Source
SiF		1.6011	857	5.57	Exp. [1]
		1.6196	833	6.07	B3LYP
		1.5997	863	6.14	CCSD(T) [88]
				5.98	Exp. [57]
SiCl		2.058	536	3.85	Exp. [1,2]
		2.0880	507	4.30	B3LYP
		2.0568	535	4.47	CCSD(T) [88]
				4.42	Exp. [56]
He_2^+		1.0808	1698	2.36	Exp. [1]
		1.1453	1360	3.27	B3LYP
		1.0805	1701	2.35	CCSD(T)
Cl_2^-		(2.65)[a]	(249)[a]	1.26	Exp. [1,35]
		2.7167	199	1.58	B3LYP
		2.5526	271	1.29	CCSD(T) [88]
MgO	$^3\Pi$	1.870	648		Exp. [44]
	$X^1\Sigma^+$	1.7490	785	(3.53)[a]	Exp. [1]
	$^1\Sigma^+$	1.7389	821		B3LYP
	$X^3\Pi$	1.8882	626	2.37	"
	$X^1\Sigma^+$	1.7508	821	4.66[b]	ACPF [88]
				2.70[c]	"
	$X^1\Sigma^+$			2.56 ± 0.2	Exp. [44]

[a] Uncertain experimental values

[b] Spectroscopic dissociation into $^1S(Mg) + {}^1D(O)$

[c] Thermodynamic dissociation into $^1S(Mg) + {}^3P_2(O)$

ferent value for the bond length is suggested [88]. Although we generally tend to trust CCSD(T) calculations, Cl_2^- could be one of the rare demanding systems for this approach as is chloryl chloride, $ClClO_2$. This compound was investigated by rotational spectroscopy where the Cl–Cl bond length (r_e) turned out to be 2.1921 Å [89]. B3LYP calculations yielded a considerably larger value of 2.244 Å, but *ab initio* CCSD(T) calculations failed dramatically with 2.279 Å [89].

Another difficult molecule is MgO. Experiments propose a $^1\Sigma^+$ ground state with an uncertain dissociation energy of 3.53 eV [1]. B3LYP calculations yield a $^3\Pi$ ground state with a dissociation energy of only 2.37 eV. The deviation of 1.16 eV cannot be explained by the reversed electronic states because their relative energies differ by only 0.46 eV. ACPF *ab initio* calculations revealed two dissociation energies (cf. footnotes in Table 8). Later, an experimental thermodynamic dissociation energy (all atoms in their ground states) was found in the literature [44], which is in accordance with B3LYP as well as the ACPF calculations. Thus, the MgO problem is solved.

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