Alkali and Alkaline Earth Metal Compounds: Core-Valence Basis Sets and Importance of Subvalence Correlation

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Abstract

Core-valence basis sets for the alkali and alkaline earth metals Li, Be, Na, Mg, K, and Ca are proposed. The basis sets are validated by calculating spectroscopic constants of a variety of diatomic molecules involving these elements. Neglect of (3s,3p) correlation in K and Ca compounds will lead to erratic results at best, and chemically nonsensical ones if chalcogens or halogens are present. The addition of low-exponent p functions to the K and Ca basis sets is essential for smooth convergence of molecular properties. Inclusion of inner-shell correlation is important for accurate spectroscopic constants and binding energies of all the compounds. In basis set extrapolation/convergence calculations, the explicit inclusion of alkali and alkaline earth metal subvalence correlation at all steps is essential for K and Ca, strongly recommended for Na, and optional for Li and Mg, while in Be compounds, an additive treatment in a separate ‘core correlation’ step is probably sufficient. Consideration of (1s) inner-shell correlation energy in first-row elements requires inclusion of (2s,2p) ‘deep core’ correlation energy in K and Ca for consistency. The latter requires special CCVnZ ‘deep core correlation’ basis sets. For compounds involving Ca bound to electronegative elements, additional d functions in the basis set are strongly recommended. For optimal basis set convergence in such cases, we suggest the sequence CV(D+3d)Z, CV(T+2d)Z, CV(Q+d)Z, and CV5Z on calcium.
I. INTRODUCTION

The rate-determining step in accurate wavefunction *ab initio* calculations is the determination of the correlation energy. Moderately reliable methods like CCSD (coupled cluster with all single and double substitutions[1]) have theoretical CPU time scalings \( \propto n^2N^4 \), where \( n \) and \( N \) represent the numbers of electrons and basis functions, respectively. For the CCSD(T) (i.e., CCSD with a quasiperturbative estimate of the effect of connected triple substitutions[2]) method — which has been termed the “gold standard of quantum chemistry” (T. H. Dunning) — the corresponding scaling is \( \propto n^3N^4 \).

For this reason, the idea of only including the ‘chemically relevant’ valence electrons in the correlation problem and constraining the inner-shell or ‘core’ orbitals to be doubly occupied gained currency early on. Bauschlicher et al.[3] were the first to propose a partitioning of the inner-shell correlation energy into a core-core (CC) component — involving excitations exclusively out of the inner-shell orbitals — and a core-valence (CV) component — involving simultaneous excitations out of the valence and inner-shell orbitals. While, at least in elements with a large core-valence gap (see below), the CC component can be expected to roughly cancel between a molecule and its separated atoms, the CV component may affect chemically relevant molecular properties to some degree.

Over time, it has become recognized that the inclusion of inner-shell correlation — even in first-row systems — is important for accurate binding energies (e.g. [4, 5]), molecular geometries (e.g.[4]), and harmonic frequencies (e.g. [4]). The treatment of inner-shell correlation requires special basis sets which not only have additional radial flexibility, but also include ‘hard’ or ‘tight’ (i.e., high-exponent) \( d, f, \ldots \) functions in order to cover angular correlation from the inner-shell orbitals. Special basis sets of this type have been developed, such as the cc-pCV\( n \)Z (correlation consistent polarized core-valence \( n \)-tuple zeta) basis sets of Woon and Dunning[6] for B–Ne, the MT (Martin-Taylor[7]) and MTsmall[8] basis sets for Li–Ar, the rather small G3large basis set[9] of Pople and coworkers for the main group elements of the first three rows, and very recently the cc-pwCV\( n \)Z (i.e. core-valence weighted cc-pCV\( n \)Z) basis sets of Peterson and Dunning[10] for B–Ne and Al–Ar.

While the CC+CV contribution to absolute correlation energies may rival or exceed the valence contribution, its differential contribution to the molecular binding energy is generally small compared to the SCF and valence correlation contributions (typically less than
1% for 1st-row systems). For that reason — as well as the formidable cost of core correlation calculations — computational thermochemistry schemes (e.g. G3 theory[9], W1/W2 theory[8, 11]) that account for inner-shell correlation generally treat the latter as a small additive contribution obtained with a relatively compact core correlation basis set. (The finding[8] that connected triple substitutions are surprisingly important for CV contributions ensures that the core correlation step often is the rate-determining one for benchmark thermochemistry calculations, particularly beyond the first row of the Periodic Table.) Recently, some attempts have been made to replace the core correlation step by bond additivity approximations[12, and references therein], and promising results have been obtained[13] by means of core polarization potentials[14].

Despite repeated warnings in the literature against the practice (e.g., by Taylor[15], by one of the present authors[4], and by Woon and Dunning[6]), core correlation is often included — for technical reasons or ‘because it cannot hurt’ — in calculations using basis sets (e.g. the standard Dunning correlation consistent basis sets[16, 17], which are of minimal basis set quality in the inner-shell orbitals) which are not adapted for nonvalence correlation. This can often cause errors on computed properties well in excess of the basis set incompleteness error: For instance, a comparison between valence-only[18] and all-electron[19] CCSD(T)/cc-pVTZ harmonic frequency calculations on the cyclic isomer of C4 suggests core correlation contributions to the harmonic frequencies of up to 50 cm\(^{-1}\), a factor of five more than the true correction obtained[18] with a core correlation basis set.

For the elements B–Ne and Al–Ar, the gap between valence and inner-shell orbital energies is large enough that a conventional core-valence separation of the orbital energies is easily made. Things are less simple further down the periodic table. Bauschlicher[20, 21] noted that for gallium and indium halides, the valence (2s) orbitals of the halogen are below the Ga(3d) or In(4d) ‘core’ orbitals in energy. At the very least, these d orbitals should be added to the correlation space; suitable basis sets for this purpose have been developed by Martin and Sundermann[22] for Ga and Ge, and by Bauschlicher[21] for In.

But similar issues arise with Group 1 and 2 elements. Radom and coworkers[23, 24] recently noted catastrophic failures of G2 theory and related methods in predicting the heats of formation of various alkali and alkaline earth metal oxides and hydroxides: for example, the binding energy of K\(_2\)O is underestimated by no less than 256 kJ/mol! Upon correlating all electrons, this error decreases to 60 kJ/mol, which is further decreased to 17
kJ/mol when more sophisticated electron correlation methods are used. Inspection of an atomic orbital energy table quickly reveals why: the oxygen 2s and 2p valence orbitals lie below the potassium 3s and 3p inner-shell orbitals, rendering the conventional separation between ‘valence’ and ‘core’ orbitals essentially meaningless. Inclusion of Group 1 and 2 subvalence correlation — termed ‘relaxed inner valence’ (RIV) by Rados and coworkers — may in fact be the appropriate treatment, not just for K (and Ca) compounds, but for alkali and alkaline earth metal compounds in general. (One of the first papers to recognize the importance of inner-shell correlation for alkali metals may have been that by Liu and coworkers.)

This problem is far from academic, considering the great importance of K\(^+\), Ca\(^{2+}\), Na\(^+\), and Mg\(^{2+}\) complexes in molecular biology. In addition, a number of these interactions (e.g., of the cation-\(\pi\) type) are not necessarily amenable to density functional treatments without validation of some kind by means of ab initio methods. Clearly, the availability of high-quality core-valence basis sets for the elements Li, Be, Na, Mg, K, and Ca would benefit the high-accuracy computational thermochemistry and spectroscopy communities as well as biomolecular modelers. The purpose of the present work is the development and validation of CVnZ (core-valence n-tuple zeta, n=D, T, Q, 5) basis sets for these elements.

II. COMPUTATIONAL DETAILS

All electronic structure calculations carried out in the present work were carried out using the MOLPRO 2000.1 and 2002.3 program systems running on SGI Origin 2000 (12 ×MIPS R10000, 300 MHz and 4 ×MIPS R10000, 195 MHz, IRIX 6.5) and Compaq ES40 (4 ×EV67, 667 MHz, Tru64 Unix 4.0f) minisupercomputers, as well as Compaq XP1000 (EV6, 500 MHz, Tru64 Unix 4.0f) and dual Intel Xeon (1.7, 2.0 and 2.4 GHz, RedHat Linux 7.2 and 7.3) workstations.

Unless explicitly noted otherwise, energy calculations were carried out at the CCSD(T) level; for open-shell systems, single-determinant ROHF reference functions were used, but the definition of the CCSD(T) energy according to Watts et al. was employed throughout.

Validation calculations on diatomic molecules were carried out as follows. Energies were computed at 21 equidistant points around the putative bond distance with interpoint spacings of 0.01–0.03 Å, depending on the curvature of the surface. Energies at these points
were converged as precisely as feasible, with integral evaluation thresholds being tightened as necessary. Polynomials of increasing order were then fit through the points, and the significance of the additional order terms subjected to a Fisher-Snedecor test. The expansion was truncated at the point where the two-way significance of the next higher order dropped below 99%. The retained expansion was generally of order between six and eight. The minimum of this curve was then sought by means of a Newton-Raphson method, and the curve re-expanded around the minimum. A Dunham analysis was then carried out on the final curve. The computed dissociation energies at 0 K, $D_0$, reported in the tables include anharmonic zero-point corrections from the computed $\omega_e$ and $\omega_ex_e$ at the same level of theory.

As for the accompanying basis sets, standard cc-pV$n$Z basis sets were used throughout on H. For O and F, aug-cc-pV$n$Z basis sets were used in valence calculations and aug-cc-pCV$n$Z basis sets in calculations where the O and F (1s) cores were correlated. For S and Cl, the aug-cc-pV($n + d$)Z basis sets of Wilson et al. were used in valence calculations, and the cc-pCV$n$Z basis sets of Peterson in calculations where the (2s,2p) cores of these elements were correlated.

Where deemed necessary, scalar relativistic effects were assessed by means of CCSD(T) calculations within the Douglas-Kroll-Hess approximation as implemented in MOLPRO 2002.3.

### III. OPTIMIZATION OF CV$n$Z BASIS SETS

#### A. General procedure

The basis set optimizations were carried out using a Fortran program developed in-house. Derivatives were obtained numerically using central differences, yielding both the gradient and the diagonal of the Hessian. The step thus obtained — essentially Newton-Raphson with neglect of off-diagonal Hessian elements — was combined with a Brent line search. Our experience with this simple but fairly robust optimization algorithm is quite good as long as optimization parameters are not too strongly coupled. In the presence of significant coupling, DIIS (Direct Inversion of the Iterative Subspace) dramatically sped up convergence.

Finite difference step sizes were made roughly proportional to the parameters themselves,
and increased as necessary if the parameter surface in the affected direction was found to be particularly ‘flat’.

Some additional optimizations were carried out using an adaptation of the DOMIN program by P. Spellucci\textsuperscript{36}, which is an implementation of the BFGS (Broyden-Fletcher-Goldfarb-Shanno) variable-metric method. Numerical derivatives of order two, four, and six were used: the lower orders until an approximate minimum was reached, after which the optimization was refined using the higher orders. In most cases, however, the simple procedure outlined above appeared to be more robust.

For the purposes of the optimization (and since only very small systems are involved), integral evaluation, SCF and CI convergence thresholds in MOLPRO were tightened to essentially machine precision. Basis set parameters were converged to at least four significant digits, and five where at all possible.

In cases where many primitives of a particular angular symmetry are required, we initially constrained these functions to follow an even-tempered sequence \( \zeta_i = \alpha \beta^{(i-n-1)/2} \), where \( n \) is the total number of primitives. Only when optimum \( \alpha \) and \( \beta \) had been reached were the individual exponents optimized further without any constraints. If a set of \( (n-1) \) primitives of that symmetry was already available (\textit{in casu}, from a previously optimized smaller basis set), the geometric mean of their exponents was taken as the starting value for \( \alpha \), and the arithmetic mean of the ratios between successive primitives as the initial value for \( \beta \).

A few ‘checks and balances’ can generally be applied to the final exponents:

1. within a row, the geometric mean of the exponents should increase roughly as \((Z^*)^2\), where \( Z^* \) is the ‘shielded’ nuclear charge (first Ahlrichs-Taylor rule\textsuperscript{37});

2. exponents in a larger set (e.g. 3\( d \)) should mesh with the next smaller set (e.g. 2\( d \));

3. the ratio of successive exponents in a set should be about two or higher, and all gaps within the core or valence parts should roughly be of the same order;

4. the geometric mean of the exponents for each angular momentum should roughly increase by a factor of 1.2 for each step up in \( L \) (second Ahlrichs-Taylor rule\textsuperscript{37}).
B. Li and Be

For Li and Be, the ‘unofficial’ cc-pV\textsuperscript{n}Z basis sets of Feller\[^{38}\] supplied in the MOLPRO 2000.1 basis set library were taken as starting points. The quantity optimized for is the (\textsuperscript{1}s) correlation energy at the CISD level for the Li(\textsuperscript{2}S) and Be(\textsuperscript{1}S) ground states, respectively. This happens to be equivalent to \(E[\text{CISD, full}] - E[\text{SCF}]\) for Li, but is equal to \(E[\text{CISD, full}] - E[\text{CISD, valence}]\) for Be.

There exists a tradition of optimizing basis sets for correlated calculations at the CISD level, since CISD is a variational method. However, optimizations for the CCSD or CCSD(T) counterparts of the abovementioned correlation energies yield very similar basis sets, which would have been of identical quality in molecular calculations. (A table of these exponents for the CVDZ, CVTZ, and CVQZ cases can be found in the Supplementary Material\[^{39}\].)

By analogy with the cc-pCV\textsuperscript{n}Z basis sets for B–Ne\[^{40}\], 1\textsuperscript{s}1\textsuperscript{p}, 2\textsuperscript{s}2\textsuperscript{p}1\textsuperscript{d}, 3\textsuperscript{s}3\textsuperscript{p}2\textsuperscript{d}1\textsuperscript{f}, and 4\textsuperscript{s}4\textsuperscript{p}3\textsuperscript{d}2\textsuperscript{f}1\textsuperscript{g} sets of primitives were added to the cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets, respectively. Successive angular momenta were optimized individually, after which the complete set of exponents was further optimized together.

Multiple local minima exist for the larger sets, and care was taken to ensure that the final optimized basis set reflects the most ‘contiguous’ (or most ‘even-tempered’) solution in the sense of having no obvious ‘gaps’ between exponents.

Aside from this issue, the basis set optimizations proceeded uneventfully.

C. Na and Mg

Likewise, for Na and Mg, unpublished cc-pV\textsuperscript{n}Z basis sets of Feller\[^{38}\] were taken as the starting point. In this case, we optimized for the 2\textsuperscript{s}2\textsuperscript{p} correlation energy, found as \(E[\text{CISD, 2s2p3s}] - E[\text{CISD, 3s}]\) for Mg and as simply \(E[\text{CISD, 2s2p3s}] - E[\text{SCF}]\) for Na. Note that the 1\textsuperscript{s} orbitals are constrained to be doubly occupied throughout: not only will the effect of this 'deep core' orbital on chemically significant properties be negligible, but including it in the optimization would bias the exponents towards the large — but chemically quite invariant — core-core correlation energy rather than the chemically more significant 2\textsuperscript{s}2\textsuperscript{p} core-core and core-valence correlation energies.

Since the highest core correlation orbital is of \textit{p} symmetry in this case, the basis sets
are rather larger, involving addition of \(1s1p1d, 2s2p2d1f, 3s3p3d2f1g, 4s4p4d3f2g1h\) core correlation sets to the cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z sets, respectively.

For the CV5Z basis sets for Na and Mg, simply optimizing a set of core correlation \(s\) functions leads to such serious near-linear dependence problems that the basis would in practice be unusable. For want of an alternative, we simply uncontracted an additional four \(s\) primitives instead.

### D. \(K\) and \(Ca\)

The core-valence gap in Ca, and particularly K, is so small that the optimization of regular cc-pV\(n\)Z basis sets would be of largely academic interest. Feller and coworkers previously published CVDZ, CVTZ, and CVQZ basis sets for K\[41\]; the \(sp\) exponents for the CVDZ and CVTZ basis sets were taken from (15s,12p) and (18s,15p) basis sets, respectively, of Ahlrichs and coworkers\[42\], while those for the CVQZ basis set were taken from the Partridge-1 set\[43\], which is of (23s,19p) uncontracted size.

Initially we employed these basis sets unaltered, and merely added a CV5Z basis set. This was obtained as follows, starting from the Partridge-3 basis set:

- the basis set was contracted to minimal (i.e. \([4s3p]\)) in an atomic calculation on the ground state
- the four outermost \(s\) and \(p\) primitives each were decontracted
- \([4d3f2g1h]\) functions were optimized at the valence-only CISD level for the \(K_2\) molecule at its experimental bond distance, yielding an intermediate cc-pV5Z basis set
- core correlation functions were obtained by optimizing the atomic \(E[\text{CISD},3s3p4s]-E[\text{SCF}]\) energy. The optimization of the \(s\) and \(p\) functions was plagued by insurmountable near-linear dependence problems, and we ended up merely decontracting an additional four primitives of \(s\) and \(p\) symmetries each. In addition, a crossover occurred between the highest \(d\) exponent of the underlying cc-pV5Z basis set and the lowest \(d\) exponent required for the inner-shell correlation, and it was decided to merely keep the outermost three \(d\) primitives constant while optimizing all five remaining \(d\) primitives for \(3s3p\) correlation.
Thus, our original CV5Z basis set was obtained. However, as evidenced in Table II, basis set convergence of properties for K_2 and KH was less than satisfactory. In particular, inspection of the dissociation energy as a function of the basis set reveals that for K_2, the CVTZ, CVQZ, and CV5Z results are nearly collinear, which is obviously undesirable. For this reason, the d, f, . . . exponents of the K CVTZ and CVQZ basis sets were reoptimized in the same manner as the CV5Z basis set. In the process we found the ‘valence correlation’ d and f exponents in the original Feller basis sets to be excessively ‘tight’, and with the adjusted basis sets (denoted ‘version 0.1’ in Table II), increases of 6.5 and 7.0 kJ/mol are seen in the CVTZ and CVQZ D_0 values. Other molecular constants are also affected quite significantly. While the Feller CVTZ and CVQZ were not found to be as problematic for the other K compounds considered in this work, they are clearly unsuitable for K_2 or any other system with similar long-distance bonding.

Analogously, we optimized CVnZ (n=D,T,Q,5) basis sets for Ca, starting from Ahlrichs 14s9p, Partridge-1 20s12p, Partridge-2 23s16p, and Partridge-3 26s16p primitive sets. Initial attempts to optimize basis sets for the 3P atomic excited state (analogously to the sp-hybridized state of Be) yielded exceedingly poor basis set convergence of molecular properties, and these basis sets were abandoned in favor of 1S ground-state optimized basis sets. (We also attempted optimizations in the CaH_2 molecule, and found basis set parameters obtained there to be very similar to those for the 1S atomic ground state.) Valence correlation functions were optimized for the valence correlation energy of the ground-state calcium atom, and core-valence functions for E[CISD,3s3p4s]-E[CISD,4s]. For the CVQZ and CV5Z basis sets, the optimized ‘valence’ and ‘subvalence’ d and f shells interlock, and as a result only the outermost 2d2f were held at their valence-optimized values and the remainder reoptimized for inner-shell correlation. No such issues arose with the g and h functions. Once again, basis set convergence of molecular properties (e.g. for CaH, but also for other diatomics, not displayed here) was found to be somewhat unsatisfactory.

For both atoms, we then optimized a sequence of four ‘stretch-tuned’ basis sets [44], i.e. basis sets in which the exponents of each angular momentum obey the following four-parameter relation:

$$\ln \zeta_n = \alpha + n(\beta + (n-1)(\gamma + (n-2)\delta))$$  \hspace{1cm} (1)

(A total of only eight parameters thus had to be optimized for each basis set.) The particular sequence of contraction sizes chosen was (20s12p), (22s14p), (24s16p), and (26s18p). The
valence and inner-shell correlation functions were optimized as before.

These basis sets (denoted ‘version 0.2’ in Table I) appeared to have better convergence properties. However, something was clearly still not satisfactory. For instance, basis set convergence for the ionization potentials of K and Ca atoms was found to be atypically slow (Table II).

It then occurred to us that, as the 4s orbital of these atoms is very diffuse, the atom-optimized p functions may be too ‘tight’ (as they were optimized for atoms with vacant 4p orbitals) to contain suitable first polarization/angular correlation functions for the outer part of the 4s orbital. This assumption was verified by optimizing single ‘probe’ basis functions of various symmetries on top of CVnZ basis sets held constant. (Only valence electrons were correlated, as otherwise the functions would have fallen into the ‘gravity well’ of the inner-shell electrons.) A very noticeable lowering of the total energy was seen upon adding a single p function, the optimum exponent of which indeed turned out to be ‘looser’ than any of the existing p functions. An additional ‘loose’ p function led to a further improvement for the K CVnZ (n=D,T,Q) basis sets, but not for the K CV5Z basis set (the outer p primitive of which is already quite ‘loose’) or any of the Ca basis sets. Consequently, the valence correlation parts of the CVnZ basis sets were reoptimized with two and one additional p functions added, respectively, for K and Ca, and afterwards the inner-shell part was reoptimized for consistency. Thus our final CVnZ basis sets were obtained. As seen in Table II, basis set convergence of molecular parameters is now satisfactory. For IP(K) and IP(Ca), nearly exact values are now obtained (Table II).

Since the primitive K and Ca basis sets may be somewhat bulky for some applications, we have also generated SDB-CVnZ basis sets, which are combinations of the valence and subvalence parts of the CVnZ basis sets with small-core Stuttgart-Dresden-Bonn [45] relativistic effective core potentials. The latter replace the (1s2s2p) electrons. Unlike the situation with large-core basis set where reoptimization of the basis set is essential [22], we have kept all exponents at their all-electron values and merely ‘pruned’ and recomtracted the basis set. Specifically, the atomic SCF calculation was repeated with the (1s2s2p) orbitals replaced by the SDB pseudopotential denoted ‘ECP10MWB’. Then all primitives with absolute coefficients of less than 10^{-5} in any valence orbitals were deleted, and the orbitals recomtracted.

All basis sets obtained in this work are available in machine-readable form (Gaussian and
MOLPRO formats) as supplementary material to the present paper. Contracted basis set sizes and numbers of basis functions for each element are given in Table I.

IV. VALIDATION FOR DIATOMIC MOLECULES

A. Diatomic metal hydrides

Since hydrogen has no core electrons, there are no differential core-core contributions (just core-valence) to the molecular properties. Computed and experimental data for the diatomic hydrides are given in Table IV.

As noted previously, the inner-shell contribution to the LiH spectroscopic constants is quite appreciable, as can be expected from the small Li(1s)-H(2s) gap of about 2 a.u. We note that the CCSD(T, riv)/CV5Z results reproduce the Born-Oppenheimer bond distance and harmonic frequency to within 0.0002 Å and 0.2 cm$^{-1}$, respectively. Neglect of Li(1s) correlation leads to errors of 0.012 Å and 13.5 cm$^{-1}$, respectively. Nevertheless, the contribution to $D_0$ does not exceed 1.2 kJ/mol.

The corresponding core-valence gap for BeH is almost doubled, which translates into substantially reduced core-valence contributions (relatively speaking) to $r_e$ and $\omega_e$. Interestingly, the contribution to $D_0$ reaches nearly 2 kJ/mol.

In contrast, the Na(2p)-H(1s) gap narrows to no more than 1 a.u., and in NaH we see inner-shell correlation contributions of 33 cm$^{-1}$ to $\omega_e$ and 0.035 Å to $r_e$. Interestingly, once more $D_e$ is nearly unaffected. Once more, the CCSD(T, riv)/CV5Z results are in excellent agreement with experiment for the spectroscopic constants: applying a W2-type extrapolation for $D_0$ results in a value of 182.35 kJ/mol, within 0.3 kJ/mol of experiment.

Given that the Mg(2p)-H(1s) gap is not dissimilar from the corresponding one in LiH, it is not greatly surprising that the importance of core-valence contributions is again much smaller than in NaH. However, the 8 kJ/mol contribution to $D_0$ is considerably more significant.

In KH, the K(3p) and H(1s) orbitals are closer than 0.5 a.u., and the contributions of nearly 0.1 Å and 44 cm$^{-1}$ to $r_e$ and $\omega_e$, respectively, clearly suggest that any sort of ‘valence correlation only’ calculation on a K compound should be viewed with great suspicion. Note that the core-valence contribution to $D_0$ is negative in this case, as was previously found.
(e.g. \[12\]) for aluminum and silicon hydrides.

In comparison, the Ca(3p)–H(1s) gap widens to 0.84 a.u., and core-valence effects on the molecular properties are mitigated accordingly. Like for MgH and KH, inner-shell correlation in fact slightly reduces the dissociation energy.

With the exception of KH and CaH, the differential core-valence contributions appear to have converged with respect to the basis set at the CVQZ stage. This in itself satisfies a minimum requirement for treating the inner-shell correlation contribution separately, something which is definitely inappropriate for KH.

On the whole, agreement between CCSD(T,riv)/CV5Z and experiment can only be described as quite satisfactory. For systems other than LiH and NaH, imperfections in the CCSD(T) electron correlation method may account for most of the remaining discrepancy between computed and observed harmonic frequencies\[46\].

\section*{B. Metal diatomics}

The alkaline earth metal dimers (particularly Be\(_2\)) exhibit such severe multireference character that they warrant studies in themselves (which would, however, focus on electron correlation methods rather than basis sets, see e.g.\[47\] and references therein). Results for species other than Be\(_2\) can be found in Table VI.

In Li\(_2\), subvalence correlation accounts for 0.024 Å, which is sizable by spectroscopist’s standards. In Na\(_2\), this is drastically increased to nearly 0.1 Å, and reaches a whopping 0.23 Å in K\(_2\). Interestingly, these contributions are quite close to double their metal hydride counterparts. As expected, LiNa and NaK represent scenarios intermediate between the homonuclear diatomics of the constituent elements. Changes in \(\omega_e\) are modest in absolute numbers, but for these molecules represent relative errors of up to 5%. It is quite clear however that, with the possible exception of Li\(_2\), inclusion of subvalence correlation is essential for reliable molecular parameters. Once again we see, however, that bond energies are only affected mildly: 0.8 kJ/mol in Li\(_2\), 1.7 kJ/mol in LiNa, 1.6 kJ/mol in Na\(_2\), and only 0.5 kJ/mol in K\(_2\).

Once again, a basis set of CVQZ quality appears to be close to convergence for the differential core-valence effects.

Effects for Mg\(_2\) and Ca\(_2\) are considerably milder than for their alkali neighbors, yet (3s, 3p)
correlation reduces the Ca$_2$ bond distance by 0.07–0.08 Å, not negligible by any reasonable standard. The discrepancies between theory and experiment for Mg$_2$ primarily reflect the inadequacy of the CCSD(T) method for this highly multireference system. In contrast, Ca$_2$ yields quite satisfying results compared to experiment.

Agreement between our best calculations and experiment can only be described as excellent for Li$_2$. The same would be true of Na$_2$ if it were not for the bond length which is still 0.003 Å too long at the CCSD(T,riv)/CV5Z level. However, at the DK-CCSD(T)/CVQZ level, we find a scalar relativistic correction to the bond length of -0.006 Å. (If this correction would seem to be exaggerated, we note that the Na$_2$ potential curve is quite flat, and that already for OH$^-$ and HF, scalar relativistic corrections were found to be required for spectroscopic-quality results.) In K$_2$, our best calculated results are likewise in excellent agreement with the experimental spectroscopic data except for $r_e$, which is calculated to be 0.014 Å longer than the observed value. At the DK-CCSD(T)/CVQZ level, we find a relativistic contribution of -0.013 Å to the bond length, which explains most of the discrepancy. In addition, the (2s, 2p) ‘deep core’ orbitals are energetically in the same range as the (1s) orbitals in C and N, so it cannot be entirely ruled out that ‘deep core’ correlation may affect molecular properties in K compounds.

We optimized a CCVTZ (deep core valence triple zeta) basis set for K. In these calculations, the CVTZ basis set was held constant and exponents of 2s2p2d1f basis functions optimized for $E[\text{CISD},2s2p3s3p4s] - E[\text{CISD},3s3p4s]$, i.e. for deep-core correlation energy taken in isolation. As can be seen in Table III, these exponents are obviously much ‘tighter’, by almost an order of magnitude, than those required for subvalence correlation. Hence, any ‘deep core’ result in a mere valence and subvalence CV$n$Z (let alone a valence-only cc-pV$n$Z set) should be regarded with skepticism at best.

The only change of note we see in the molecular properties when using this CCVTZ basis set for K$_2$ is a shortening of the K–K bond by another 0.0018 Å. We also attempted to optimize a CCVQZ basis set but ran into insurmountable near-linear-dependence problems; however, the CCVTZ result should at least give an indication of the (fairly modest) magnitude of this effect.
C. Diatomic metal halides

This set of molecules is particularly relevant because of the deep-lying valence s orbitals on the halogen atoms. Relevant results are collected in Table VII.

Firstly, for LiF the contribution of Li(1s) correlation to the binding energy is somewhat more noticeable (4 kJ/mol). Its inclusion also causes a contraction of the bond by 0.015 Å and an increase in $\omega_e$ of 12 cm$^{-1}$. The further effect of permitting F(1s) correlation is nearly negligible in comparison. The Cl(2s,2p) correlation effect is somewhat more noticeable but still Li(1s) correlation accounts for the lion’s share of the changes.

The F(2s) and Na(2p) orbitals are nearly degenerate, and hence one would expect valence-only calculations on NaF to be problematic, to say the least. Nevertheless, while the effect of Na(2s,2p) correlation on the molecular constants is quite noticeable and its inclusion clearly essential for accurate calculations, the results obtained are not outright nonsensical. Of course, considering the difference in electronegativity between the elements, the combination of Na$^+$ and F$^-$ would yield a more appropriate (if perhaps extreme) ‘atoms in molecules’ picture — and the corresponding orbital energy gap in this admittedly extreme scenario is 0.72 a.u. with the Partridge 3 basis set. The corresponding ‘ionic’ gap for NaCl amounts to 1.07 a.u., explaining why also for NaCl, valence-only results are not totally unreasonable.

The person carrying out calculations on KF and KCl has no such luck. The inclusion of K(3s3p) correlation shifts $\omega_e$ in KF upwards by no less than 20%, and the contribution to $D_e$ is seen to be on the order of 170 kJ/mol. In fact, the ‘valence’ results are better described as referring to correlating the z component of K(3p) and freezing the F(2s), which obviously makes no chemical sense at all. The valence-computed dissociation energy of KCl agrees deceptively well with experiment, but an error of 0.3 Å in the bond distance and of a factor of three in the anharmonicity constant should discourage any quantum chemist from performing valence-only calculations on this type of species.

While obviously significant for spectroscopic purposes, the effects of metal subvalence correlation in MgF and MgCl are clearly less prominent than in NaF and NaCl, respectively, and with the beryllium halides, one clearly could ‘get away’ with a differential treatment. In contrast, in CaF a calcium subvalence contribution to $D_0$ of 180 kJ/mol is found, not to mention +46 cm$^{-1}$ on $\omega_e$ and a factor of two on $\omega_e x_e$. Oddly, the effect on the bond length is comparatively small (0.04 Å). The opposite scenario is seen for CaCl, with a $\Delta r_e$ of 0.1 Å.
but otherwise not outlandishly erroneous values for the other spectroscopic constants. CaF and CaCl results resemble more the potassium halides.

And once again, the CCSD(T, riv)/CV5Z results agree as well with experiment as can reasonably be expected.

We have also considered calculations in which subvalence correlation on the halide was permitted. However, for K and Ca compounds with \( \{ \text{C, N, O, F} \} \), the (1s) orbital of these latter elements is in fact below the K(2s,2p) ‘deep core’ orbitals in energy, and therefore any such calculation will require the use of CC\( n \)Z ‘deep core’ basis sets on the metal. Such calculations are sufficiently costly that one might want to limit them to single-point energy calculations in high-accuracy thermodynamic work. For MCl, the most noticeable effect of including (2\( s, 2p \)) subvalence correlation on chlorine is a contraction of \( r_e \) by 0.003 Å.

D. The metal chalcogenides

We will primarily focus on the oxides. Results can be found in Table VIII.

Clearly, changes of 13 cm\(^{-1}\) and 6 kJ/mol, respectively, for \( \omega_e \) and \( D_e \) of BeO suggest the importance of metal (1s) correlation in this system; contributions from O(1s) correlation are an order of magnitude less important. Note that the experimental data can be reproduced almost exactly at the CCSD(T, all)/CV5Z level, despite BeO having pronounced multireference character and in fact being on the borderline of applicability of CCSD(T) (see e.g.[49]). In the isovalent BeS system, Be(1s) correlation is still noticeably more important than S(2s,2p) correlation, although the difference is not as pronounced as its counterpart in BeO.

Changes between valence-only and RIV treatment of 0.017 Å in \( r_e \)(MgO) and 23 cm\(^{-1}\) in \( \omega_e \)(MgO) speak for themselves. The MgO molecule has very pronounced multireference character, and accurate reproduction of the experimental spectroscopic constants would required an elaborate multireference treatment. Subvalence correlation effects in MgS are rather milder.

In contrast, inspection of the computed spectroscopic constants for CaO immediately reveals that valence-only calculations on this system are essentially exercises in wasting computer time. Valence-only bond distances and dissociation energies are off by a quarter of an Å, and a factor of six in \( D_0 \). Respectable agreement with experiment can however
be reached by correlating the Ca(3s,3p) electrons. Obviously, the large uncertainties in the measured dissociation energies preclude really fine comparisons with experiment: on the basis of the preceding, it can perhaps be stated that the calculated binding energies are more reliable than the experimental ones for the alkali(ne earth) metal chalcogenides.

Once again, correlating the (1s) orbital on O would require including (2s, 2p) deep-core correlation in Ca, otherwise meaningless results are obtained.

E. Additional \textit{d} functions on Ca

Wesolowski et al.\textsuperscript{50}, in a study of calcium oxide, observed especially poor performance for a valence-only atomic natural orbital (ANO) basis set\textsuperscript{51}. This was considerably improved when high-exponent \textit{d} functions were added. They noted that Ca\textsuperscript{+} has a low-lying \textit{2D} state only 1.7 eV above the \textit{2S} ground state, and showed that said ANO basis set over-estimates this separation by nearly a factor of three. Addition of several very high-exponent \textit{d} functions, taken from the 6-311G(2df) basis set for Ca\textsuperscript{52} (which treats the (3d) orbital on a valence footing), results in an at least semiquantitatively correct result.

As the present basis sets were developed from the ground up with inner-shell correlation in mind, they intrinsically contain high-exponent \textit{d} functions and should therefore be much less susceptible to the problem. As shown in Table IX, quite good agreement with the experimental transition energy is obtained for CVQZ and CV5Z basis sets, but the smaller basis sets leave something to be desired.

We therefore proceeded to optimize CV\textit{(n+d)}Z, CV\textit{(n+2d)}Z, and CV\textit{(n+3d)}Z basis sets in the following fashion. (Both the nomenclature and the procedure bear resemblance to the \textit{cc-pV(n+d)}Z basis sets for second-row elements\textsuperscript{32}.) All angular momenta other than \textit{d} were kept constant, as were the valence-optimized \textit{d} functions (see above). The remaining \textit{d} functions were reoptimized for inner-shell correlation with one, two, or three additional \textit{d} functions added. (In the CV\textit{(Q+d)}Z and CV\textit{(Q+2d)}Z basis sets, it was found necessary to constrain the exponents to stretch-tuned and even-tempered sequences, respectively.)

As can be seen in Table IX, the \textit{2D} \textleftarrow \textit{2S} excitation energy indeed converges considerably faster for the CV\textit{(n+d)}Z and CV\textit{(n+2d)}Z series than for the CV\textit{nZ} series. After applying a scalar relativistic correction by means of the Douglas-Kroll method in an uncontracted CV\textit{(Q+d)}Z basis sets, very good agreement with experiment can be achieved. As for the
molecular properties of CaO (Table VIII), the effect of additional \( d \) functions is quite dramatic in the CVDZ case and still quite important in the CVTZ case, but tapers off for CVQZ and becomes quite insignificant for CV5Z. We noticed similar behavior in the other CaX systems considered in this paper (Tables V, VI, and VII). Convergence as a function of the number of additional \( d \) functions appears to be approached for CV(D+3d)Z, CV(T+2d)Z, CV(Q+d)Z, and CV5Z (note particularly Table VIII). Basis set convergence of molecular properties along this sequence is clearly much smoother than for the unmodified CV\( n \)Z basis sets. This is particularly true for CaO and, to a somewhat lesser extent, for CaF, least so for CaH and Ca\(_2\) where basis set convergence was adequate to begin with.

V. CONCLUSIONS

Core-valence basis sets have been developed for the alkali and alkaline earth metals Li, Be, Na, Mg, K, and Ca. Validation calculations for a number of diatomics involving these systems reveal basis set convergence to be satisfactory.

The addition of low-exponent \( p \) functions to the K and Ca basis set is found to be essential for smooth basis set convergence of molecular properties. These functions accommodate angular correlation from the outer part of the 4s orbital.

Valence-only calculations on K and Ca chalcogenides and halides yield large errors at best, and chemically nonsensical results at worst. In general, inclusion of subvalence correlation in K and Ca compounds is absolutely essential for even reliable (let alone accurate) results, while for accurate calculations, subvalence correlation in Na (and, to a lesser extent, Li and Mg) should be included, preferably as a ‘baseline’ treatment rather than an additive correction. The latter appears to be sufficient for Be compounds. Any study that seeks to address the importance of first-row element core correlation in K and Ca compounds should also consider deep-core (2s,2p) correlation from these latter elements.

For compounds involving Ca bound to highly electronegative elements, we strongly recommend basis sets with additional \( d \) functions on Ca: our suggested sequence for basis set convergence studies would be CV(D+3d)Z, CV(T+2d)Z, CV(Q+d)Z, CV5Z.
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CVnZ and SDB-CVnZ basis sets can be downloaded at the Uniform Resource Locator [http://theochem.weizmann.ac.il/web/papers/group12.html](http://theochem.weizmann.ac.il/web/papers/group12.html) in both Gaussian and MOLPRO formats.

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By analogy with ‘even-tempered’ [53] and ‘well-tempered’ [54] basis sets, the term ‘stretch-
tuned’ is borrowed from the musician’s lingo. It refers to the habit of piano tuners, in order to reduce strain on the frame, to deviate from ‘even-tempered’ tuning at the low and high ends of the keyboard. Specifically, low notes are tuned flat, and high notes sharp, relative to their even-tempered pitch.

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|       | $r_e$ (Å) | $\omega_e$ (cm$^{-1}$) | $\omega_{exc}$ (cm$^{-1}$) | $D_0$ (kJ/mol) |
|-------|-----------|------------------------|-----------------------------|---------------|
| **KH** |           |                        |                             |               |
| CVDZ Feller       | 2.2835    | 935.7                  | 13.80                       | 124.3         |
| CVDZ version 0.1  | 2.2847    | 930.0                  | 13.87                       | 123.2         |
| CVDZ version 0.2  | 2.2673    | 960.5                  | 18.61                       | 125.4         |
| Final CVDZ (incl. +2p) | 2.3323    | 902.1                  | 11.42                       | 136.1         |
| CVTZ Feller       | 2.2382    | 998.8                  | 16.69                       | 156.7         |
| CVTZ version 0.1  | 2.2410    | 991.0                  | 17.11                       | 153.0         |
| CVTZ version 0.2  | 2.2360    | 1025.3                 | 13.64                       | 159.5         |
| Final CVTZ (incl. +2p) | 2.2591    | 976.3                  | 15.41                       | 161.2         |
| CVQZ Feller       | 2.2353    | 1002.9                 | 14.24                       | 166.0         |
| CVQZ version 0.1  | 2.2353    | 1003.5                 | 14.73                       | 165.0         |
| CVQZ version 0.2  | 2.2419    | 991.7                  | 13.93                       | 166.2         |
| Final CVQZ (incl. +2p) | 2.2479    | 979.0                  | 14.32                       | 167.8         |
| CV5Z version 0.1  | 2.2406    | 989.8                  | 15.31                       | 168.8         |
| CV5Z version 0.2  | 2.2445    | 985.3                  | 15.81                       | 169.4         |
| Final CV5Z (incl. +2p) | 2.2461    | 982.6                  | 15.84                       | 170.0         |
| Expt.$^a$ | 2.240164(10) | 986.6484(41) | 15.54 | 170.972$^b$ |
| **K$_2$** |           |                        |                             |               |
| CVDZ Feller       | 4.1250    | 77.1                   | 0.45                        | 27.5          |
| CVDZ version 0.1  | 4.1507    | 74.6                   | 0.42                        | 27.2          |
| CVDZ version 0.2  | 4.2223    | 69.9                   | 0.43                        | 24.5          |
| Final CVDZ (incl. +2p) | 4.0511    | 88.5                   | 0.29                        | 50.0          |
| CVTZ Feller       | 3.9956    | 87.2                   | 0.40                        | 36.9          |
| CVTZ version 0.1  | 3.9561    | 92.1                   | 0.32                        | 43.4          |
| CVTZ version 0.2  | 4.0180    | 78.1                   | 0.38                        | 30.9          |
| Final CVTZ (incl. +2p) | 3.9837    | 90.1                   | 0.25                        | 50.2          |
| CVQZ Feller       | 3.9434    | 91.8                   | 0.34                        | 41.7          |
| CVQZ version 0.1  | 3.9522    | 93.0                   | 0.29                        | 48.7          |
| CVQZ version 0.2  | 3.9502    | 90.9                   | 0.35                        | 44.0          |
| Final CVQZ (incl. +2p) | 3.9557    | 92.0                   | 0.33                        | 51.2          |
| CV5Z version 0.1  | 3.9440    | 92.9                   | 0.29                        | 51.6          |
| Final CV5Z (incl. +2p) | 3.9380    | 93.0x                  | 0.34                        | 52.2          |
| Expt.$^c$ | 3.92435(2) | 92.39766(47) | 0.32485(12) | 53.243(2) |

(a) Uehara, H., Horiai, K., and Konno, T., 1997, *J. Mol. Struct.* 413, 457.
(b) Ref.$^{55}$, corrected to 0 K using spectroscopic constants given to the left.
(c) Amiot, C., Vergès, J., and Fellows, C. E., 1995, *J. Chem. Phys.* 103, 3350.
TABLE II: Basis set convergence of ionization potentials of K and Ca (eV), with and without low-exponent p functions added.

|          | CCSD(T) | DK-CCSD(T) |
|----------|---------|------------|
|          |         | +2p        |            |
| CVDZ     | 4.068   | 4.108      | 4.086      |
| CVTZ     | 4.218   | 4.275      | 4.236      |
| CVQZ     | 4.300   | 4.301      | 4.317      |
| CV5Z     | 4.308   | 4.308      | 4.326      |
| CV∞Z     | 4.316   | 4.315      | 4.335      |

Basis set limits using expression [56]: \( E_\infty \approx E_L + (E_L - E_{L-1})/((L/L-1)^3 - 1) \)

(a) Handbook of Chemistry and Physics (CRC Press, Boca Raton, FL, 2001), p. 10-175.

TABLE III: Valence correlation, core-valence and deep-core correlation exponents in the CVTZ and CCVTZ basis sets for potassium.

|          | Valence | Core | Deep core |
|----------|---------|------|-----------|
| s        | 0.0181, 0.0501 | 0.346, 1.779 | 4.281, 20.055 |
| p        | 0.0275, 0.0598 | 0.529, 2.599 | 7.240, 16.761 |
| d        | 0.0599, 0.431  | 1.036, 2.586 | 9.724, 28.720 |
| f        | 0.0888       | 1.129 | 15.150    |

TABLE IV: Contracted basis set sizes and total numbers of basis functions for the CVnZ basis sets for group 1 and 2 elements

|          | CVDZ     | CVTZ     | CVQZ     | CV5Z     |
|----------|----------|----------|----------|----------|
| Li,Be    | 18       | [4s3p1d] | [6s5p3d1f] | 43       |
| Na,Mg    | 27       | [5s4p2d] | [7s6p4d2f] | 59       |
| K,Ca     | 31       | [6s5p2d] | [8s7p4d2f] | 63       |
TABLE V: Computed and observed spectroscopic constants (kJ/mol, Å, cm$^{-1}$ as appropriate) for alkali and alkaline earth metal hydrides.

|                 | $r_e$   | $\omega_e$ | $\omega_e x_e$ | $D_0$     |
|-----------------|---------|------------|----------------|-----------|
|                 | Val     | RIV        | Val            | RIV       | Val     | RIV       |
| LiH             |         |            |                |           |         |           |
| CVDZ            | 1.6191  | 1.6106     | 1369.1         | 1379.6    | 20.80   | 21.55     | 209.1     | 210.6     |
| CVTZ            | 1.6081  | 1.5994     | 1394.9         | 1400.1    | 22.72   | 22.08     | 227.6     | 228.7     |
| CVQZ            | 1.6069  | 1.5960     | 1393.1         | 1405.3    | 23.61   | 22.84     | 231.4     | 232.6     |
| CV5Z            | 1.6074  | 1.5954     | 1391.8         | 1405.7    | 22.78   | 23.21     | 232.4     | 233.6     |
| Expt.$^a$       | 1.5956  | 1.43018    | 1405.49805(76) | 23.167899(714) | 244.33, 234.354(4)$^g$ |
| BeH             |         |            |                |           |         |           |
| CVDZ            | 1.3587  | 1.3556     | 2036.1         | 2033.9    | 34.35   | 34.26     | 177.4     | 178.1     |
| CVTZ            | 1.3498  | 1.3448     | 2039.9         | 2053.3    | 35.40   | 35.79     | 191.3     | 193.1     |
| CVQZ            | 1.3458  | 1.3411     | 2054.9         | 2065.6    | 36.32   | 36.65     | 195.9     | 197.7     |
| CV5Z            | 1.3456  | 1.3407     | 2055.3         | 2065.9    | 36.57   | 36.68     | 196.8     | 198.7     |
| Expt.$^b$       | 1.3411  | 1.3556     | 2036.1         | 2033.9    | 34.35   | 34.26     | 177.4     | 178.1     |
| NaH             |         |            |                |           |         |           |
| CVDZ            | 1.9237  | 1.9078     | 1116.3         | 1115.7    | 17.41   | 17.58     | 158.0     | 158.7     |
| CVTZ            | 1.9232  | 1.8949     | 1131.6         | 1154.0    | 16.46   | 18.56     | 176.1     | 176.5     |
| CVQZ            | 1.9256  | 1.8907     | 1122.8         | 1159.3    | 10.10   | 17.89     | 179.7     | 180.2     |
| CV5Z            | 1.9235  | 1.8883     | 1137.8         | 1171.1    | 18.43   | 19.67     | 181.7     | 181.2     |
| Expt.$^c$       | 1.8870  | 1.8907     | 1116.3         | 1115.7    | 17.41   | 17.58     | 158.0     | 158.7     |
| MgH             |         |            |                |           |         |           |
| CVDZ            | 1.7442  | 1.7398     | 1468.1         | 1458.9    | 27.22   | 26.31     | 107.6     | 106.3     |
| CVTZ            | 1.7434  | 1.7332     | 1496.6         | 1499.7    | 28.36   | 28.59     | 123.3     | 120.3     |
| CVQZ            | 1.7413  | 1.7299     | 1494.5         | 1498.1    | 28.46   | 29.10     | 127.1     | 122.9     |
| CV5Z            | 1.7401  | 1.7289     | 1493.2         | 1498.8    | 28.25   | 29.31     | 128.3     | 123.5     |
| Expt.$^d$       | 1.729828(2)| 1.7332(22)| 1495.2632(84)| 129, 122.7 ± 2.9$^g$ |
| KH              |         |            |                |           |         |           |
| CVDZ            | 2.3567  | 2.3232     | 907.6          | 902.1     | 12.58   | 11.42     | 141.0     | 136.1     |
| CVTZ            | 2.3230  | 2.2591     | 950.7          | 976.3     | 14.97   | 15.41     | 167.5     | 161.2     |
| CVQZ            | 2.3241  | 2.2479     | 944.4          | 979.0     | 14.41   | 14.32     | 173.3     | 167.8     |
| CV5Z            | 2.3274  | 2.2461     | 938.8          | 982.6     | 14.81   | 15.84     | 174.8     | 170.0     |
| Expt.$^e$       | 2.240164(10)| 2.2461| 986.6484(41) | 15.54     | 179, 170.972$^g$ |

(continued on next page)
TABLE V: (continued)

| Method  | CaH          | CVDZ | CV(D+d)Z | CV(D+2d)Z | CV(D+3d)Z | CVTZ     | CV(T+d)Z | CV(T+2d)Z | CVQZ      | CV(Q+d)Z | CV5Z      | Expt.     |
|---------|--------------|------|----------|-----------|-----------|----------|----------|-----------|-----------|----------|-----------|-----------|
|         |              | 2.1453 | 2.0941   | 1231.5    | 1227.4    | 20.04    | 18.17    | 114.3     | 115.7     |          |           |           |
|         |              | 2.0539 | 1249.6   | 1227.4    | 1218.1    | 18.21    | 16.85    | 153.7     | 154.7     |          |           |           |
|         |              | 2.0323 | 1260.3   | 1227.4    | 1267.1    | 18.25    | 153.7     |           |           |          |           |           |
|         |              | 2.0227 | 1290.5   | 1227.4    | 1298.0    | 20.56    | 154.7     |           |           |          |           |           |
|         |              | 2.1344 | 2.0415   | 1253.2    | 1273.9    | 18.70    | 17.29    | 141.5     | 148.4     |          |           |           |
|         |              | 2.0204 | 1279.1   | 1227.4    | 153.7     | 16.85    | 154.7     |           |           |          |           |           |
|         |              | 2.0149 | 1283.8   | 1227.4    | 154.7     | 17.46    | 154.7     |           |           |          |           |           |
|         |              | 2.0899 | 2.0063   | 1270.4    | 1297.9    | 20.62    | 18.80    | 158.5     | 162.5     |          |           |           |
|         |              | 2.0048 | 1298.7   | 1297.9    | 162.9     | 18.72    | 162.9     |           |           |          |           |           |
|         |              | 2.0077 | 1296.9   | 1297.9    | 160.4     | 18.53    | 160.4     |           |           |          |           |           |
|         |              | 2.0062 | 1297.9   | 1297.9    | 160.8     | 18.65    | 160.8     |           |           |          |           |           |
|         |              | 2.0536 | 2.0027   | 1271.9    | 1299.1    | 18.68    | 18.93    | 169.3     | 165.2     |          |           |           |
|         | Expt.       | 2.002366(16) | 1298.3999(40) | 19.1842(28) | 164 ≤ 164.19 |

(a) (LiH) Dulick, M., Zhang, K.-Q., Guo, B., and Bernath, P.F., 1998, *J. Mol. Spectrosc.* **188**, 14.
(b) (BeH) (1) Colin, R. and De Greef, D., 1975, *Can. J. Phys.* **53**, 2142. (2) Martin, J. M. L., 1998, *Chem. Phys. Lett.* **283**, 283.
(c) (NaH) Pesl, F. P., Lutz, S., and Bergmann, K., 2000, *Eur. Phys. J. D.* **10**, 247.
(d) (MgH) Lemoine, B., Demuynck, C., Destombes, J.L., and Davies, P.B., 1988, *J. Chem. Phys.* **89**, 673.
(e) (KH) Uehara, H., Horiai, K., and Konno, T., 1997, *J. Mol. Struct.* **413**, 457.
(f) (CaH) Petitprez, D., Lemoine, B., Demuynck, C., Destombes, J.L., and Macke, B., 1989, *J. Chem. Phys.* **91**, 4462.
(g) First value from Huber and Herzberg [57], second from CRC Handbook [55], corrected to 0 K with expt. \(\omega_x\) and \(\omega_e\).
TABLE VI: Computed and observed spectroscopic constants (kJ/mol, Å, cm\(^{-1}\) as appropriate) for alkali and alkaline earth metal diatomics.

|      | \(r_e\) (Val RIV) | \(\omega_e\) (Val RIV) | \(\omega_e x_e\) (Val RIV) | \(D_0\) (Val RIV) |
|------|------------------|------------------|------------------|------------------|
| **Li\(_2\)** |                  |                  |                  |                  |
| CVDZ | 2.7284 2.6963    | 340.4 346.7      | 2.32 2.44        | 92.0 95.5        |
| CVTZ | 2.7006 2.6802    | 347.1 348.8      | 2.50 2.53        | 97.3 98.2        |
| CVQZ | 2.6984 2.6756    | 346.6 351.0      | 2.53 2.58        | 98.5 99.2        |
| CV5Z | 2.6985 2.6741    | 346.6 351.3      | 2.54 2.59        | 98.8 99.4        |
| Expt. | 2.6729 351.43    |                  | 2.610            | 100.9 107.45 \(^{+4}\) |
| **LiNa\(_2\)** |                |                  |                  |                  |
| CVDZ | 2.9679 2.9386    | 244.1 247.5      | 1.38 1.45        | 77.0 79.9        |
| CVTZ | 2.9505 2.9051    | 247.6 253.5      | 1.50 1.55        | 81.0 82.5        |
| CVQZ | 2.9496 2.8953    | 248.6 256.1      | 1.56 1.64        | 81.7 83.0        |
| CV5Z | 2.9500 2.8910    | 248.9 256.4      | 1.55 1.61        | 82.0 83.1        |
| Expt. | 2.88881(2)       | 256.4577(14)     | 1.5808(6)        | N/A, 84.728 \(\pm\) 0.001 \(^{h}\) |
| **Na\(_2\)** |                |                  |                  |                  |
| CVDZ | 3.2048 3.1829    | 149.9 152.8      | 0.80 1.48        | 65.0 67.9        |
| CVTZ | 3.1779 3.1007    | 151.7 158.4      | 0.66 0.69        | 68.4 70.9        |
| CVQZ | 3.1773 3.0884    | 151.7 158.7      | 0.69 0.74        | 68.8 70.6        |
| CV5Z | 3.1783 3.0822    | 152.1 159.3      | 0.67 0.71        | 69.1 70.7        |
| Expt. | 3.0795(1)        | 159.103(3)       | 0.7190(6)        | 69, 71.0173 \(\pm\) 0.0001 \(^{h}\) |
| **NaK\(_2\)** |               |                  |                  |                  |
| CVDZ | 3.6793 3.6072    | 115.7 118.4      | 0.45 0.44        | 58.0 59.6        |
| CVTZ | 3.6666 3.5379    | 116.6 121.3      | 0.43 0.44        | 61.3 60.9        |
| CVQZ | 3.6671 3.5185    | 116.7 122.8      | 0.44 0.44        | 61.8 61.4        |
| CV5Z | 3.6661 3.5070    | 117.0 124.0      | 0.44 0.44        | 61.9 61.9        |
| Expt. | 3.49903          | 123.993          | 0.3045           | 60, 64.089 \(\pm\) 0.008 \(^{h}\) |
| **Mg\(_2\)** |               |                  |                  |                  |
| CVDZ | 4.9450 4.8450    | 17.1 18.8        | 0.60 0.62        | 1.0 1.3          |
| CVTZ | 4.0581 4.0333    | 41.0 43.6        | 1.65 1.51        | 3.0 3.3          |
| CVQZ | 3.9748 3.9717    | 46.6 46.0        | 1.68 1.64        | 3.9 3.8          |
| CV5Z | 3.9579 3.9709    | 47.6 45.9        | 1.67 1.50        | 4.1 3.9          |
| Expt. | 3.8905           | 51.121           | 1.645            | 4.83, 7.037 \(\pm\) 0.004 \(^{h}\) |
| **K\(_2\)** |              |                  |                  |                  |
| CVDZ | 4.1626 4.0511    | 85.4 88.5        | 0.28 0.29        | 48.7 50.0        |
| CVTZ | 4.1684 3.9837    | 85.8 90.1        | 0.27 0.25        | 51.1 50.2        |
| CVQZ | 4.1694 3.9557    | 85.8 92.0        | 0.28 0.33        | 51.6 51.2        |
| DK-CVQZ | 3.9407       | 92.9            | 0.21             | 52.1             |
| CV5Z | 4.1693 3.9380    | 85.6 93.0        | 0.28 0.34        | 51.7 52.2        |
| Expt. | 3.92435(2)       | 92.39766(47)     | 0.32485(12)      | 49.6, 52.88(2) \(^{h}\), 53.243(2) \(^{g}\) |

(continued on next page)
|         | \( r_e \) | \( \omega_e \) | \( \omega_e x_e \) | \( D_0 \) |
|--------|-----------|--------------|----------------|--------|
|        | Val RIV   | Val RIV      | Val RIV        | Val RIV|
| Ca\(_2\) |
| CVDZ   | 5.0096 4.7730 | 26.8 33.8 1.11 1.23 2.5 3.4  |
| CV(D+d)Z | 4.7956    | 32.5 1.17 3.5  |
| CV(D+2d)Z | 4.7642    | 33.5 1.19 3.7  |
| CV(D+3d)Z | 4.7554    | 33.9 1.17 3.8  |
| CVTZ   | 4.5409 4.4185 | 53.6 56.1 1.05 1.07 8.3 9.0  |
| CV(T+d)Z | 4.3932    | 57.2 1.08 9.6 |
| CV(T+2d)Z | 4.3899    | 57.2 1.09 9.6 |
| CVQZ   | 4.4385 4.3440 | 60.6 60.9 1.05 1.07 10.7 11.0 |
| CV(Q+d)Z | 4.3417    | 61.0 1.07 10.9 |
| DK-CVQZ | 4.3313    | 59.1 0.99 11.0 |
| DK-CV(Q+d)Z | 4.3289    | 59.2 1.00 11.1 |
| CV5Z   | 4.4005 4.3261 | 63.0 61.5 1.08 1.07 12.1 11.5 |
| Expt.\(^i\) | 4.2773 4.277 | 64.93 65.07 1.065 1.09 12.4±1 13.1 |

(a) (Li\(_2\)) Huber and Herzberg\(^{57}\).
(b) (LiNa) Fellows, C.E., 1991, *J. Phys. Chem.* 94, 5855.
(c) (Na\(_2\)) Babaky, O. and Hussein, K. J., 1989, *Can. J. Phys.* 67, 912.
(d) (NaK) Krou-Adohi, A. and Giraud-Cotton, S., 1998, *J. Mol. Spectrosc.* 190, 171.
(e) (Mg\(_2\)) Huber and Herzberg\(^{57}\).
(f) (K\(_2\)) With CCVTZ deep-core correlation basis set and correlating all but (1s) electrons (RIV values given in parentheses):
\( r_e=3.9809(3.9827) \) Å, \( \omega_e=90.2(90.2) \) cm\(^{-1}\), \( \omega_e x_e=0.25(0.25) \) cm\(^{-1}\), \( D_0=50.3(50.2) \) kJ/mol. (g) (K\(_2\)) Amiot, C., Vergès, J., and Fellows, C.E., 1995, *J. Chem. Phys.* 103, 3350.
(h) First value from Huber and Herzberg\(^{57}\), second from CRC Handbook\(^{55}\) corrected to 0 K with expt. \( \omega_e x_e \) and \( \omega_e \).
(i) First set of values: Huber and Herzberg\(^{57}\), from Balfour, W. J. and Whitlock, R. F., 1975, *Can. J. Phys.* 53, 472; Second set of values: Vidal, C. R., 1980, *J. Chem. Phys.* 72, 1864, Bondybey, V. E. and English, J. H., 1984, *Chem. Phys. Lett.* 111, 195.
|                | $r_e$   | $\omega_e$ | $\omega_x e$ | $D_0$  |
|----------------|---------|------------|--------------|--------|
|                | Val    | RIV        | All          | Val    | RIV        | All          |
| LiF            |        |            |              |        |            |              |
| CVDZ           | 1.6074 | 1.5983     | 1.5977       | 870.6  | 876.1      | 876.9        | 8.16    | 8.18     | 8.18    |
| CVTZ           | 1.5903 | 1.5747     | 1.5741       | 885.5  | 891.2      | 891.7        | 7.79    | 7.70     | 7.74    |
| CVQZ           | 1.5817 | 1.5671     | 1.5665       | 894.4  | 906.1      | 906.6        | 8.00    | 8.12     | 8.13    |
| CV5Z           | 1.5808 | 1.5656     | 1.5650       | 895.9  | 908.0      | 908.6        | 8.04    | 8.12     | 8.14    |
| Expt.$^a$      |        |            |              |        |            |              | 1.5638648(3) | 910.57272(10) | 8.207956(46) | 570, 537 ± 21$^m$ |
| LiCl           |        |            |              |        |            |              |
| CVDZ           | 2.0900 | 2.0819     | 2.0806       | 600.9  | 607.4      | 608.7        | 3.57    | 3.97     | 3.95    |
| CVTZ           | 2.0486 | 2.0375     | 2.0351       | 626.9  | 633.1      | 634.3        | 4.26    | 4.33     | 4.34    |
| CVQZ           | 2.0430 | 2.0291     | 2.0266       | 632.2  | 640.1      | 641.0        | 4.38    | 4.45     | 4.45    |
| Expt.$^b$      |        |            |              |        |            |              | 2.0206719(2) | 642.95821(14) | 4.475085(57) | 467, 466 ± 13$^m$ |
| BeF            |        |            |              |        |            |              |
| CVDZ           | 1.4148 | 1.4083     | 1.4078       | 1190.9 | 1197.6     | 1198.9       | 8.27    | 8.52     | 8.54    |
| CVTZ           | 1.3741 | 1.3696     | 1.3690       | 1240.1 | 1245.3     | 1246.4       | 9.13    | 9.17     | 9.19    |
| CVQZ           | 1.3689 | 1.3635     | 1.3531       | 1254.8 | 1264.1     | 1264.3       | 9.30    | 9.39     | 9.40    |
| CV5Z           | 1.3678 | 1.3623     | 1.3617       | 1255.3 | 1264.5     | 1265.4       | 9.27    | 9.34     | 9.35    |
| Expt.$^c$      |        |            |              |        |            |              | 1.36075(3) | 1265.54(10) | 9.422(28) | 564, 604, 573 ± 42$^m$ |
| BeCl           |        |            |              |        |            |              |
| CVDZ           | 1.8323 | 1.8269     | 1.8251       | 817.4  | 816.5      | 817.8        | 5.12    | 4.89     | 4.89    |
| CVTZ           | 1.8165 | 1.8117     | 1.8087       | 833.1  | 837.6      | 839.6        | 4.87    | 4.90     | 4.93    |
| CVQZ           | 1.8076 | 1.8018     | 1.7989       | 839.3  | 841.5      | 846.5        | 4.91    | 4.94     | 4.94    |
| Expt.$^d$      |        |            |              |        |            |              | 1.7971 | 846.7    | 4.85(3)  |
| NaF            |        |            |              |        |            |              |
| CVDZ           | 1.9869 | 1.9485     | 1.9478       | 528.2  | 527.2      | 527.7        | 4.59    | 4.03     | 4.03    |
| CVTZ           | 1.9966 | 1.9412     | 1.9402       | 532.1  | 523.9      | 524.4        | 4.34    | 3.46     | 3.49    |
| CVQZ           | 1.9967 | 1.9318     | 1.9311       | 534.0  | 530.4      | 530.6        | 4.35    | 3.54     | 3.54    |
| CV5Z           | 1.9916 | 1.9291     | 1.9284       | 537.8  | 533.8      | 534.0        | 4.45    | 3.53     | 3.53    |
| Expt.$^e$      |        |            |              |        |            |              | 1.9259455(2) | 535.65805(21) | 3.57523(13) | (514), 516$^m$ |
| NaCl           |        |            |              |        |            |              |
| CVDZ           | 2.4278 | 2.4117     | 2.4099       | 324.8  | 345.9      | 346.8        | 1.76    | 1.79     | 1.80    |
| CVTZ           | 2.4133 | 2.3868     | 2.3845       | 346.5  | 354.2      | 354.4        | 1.62    | 1.73     | 1.73    |
| CVQZ           | 2.4064 | 2.3729     | 2.3705       | 350.6  | 360.2      | 360.7        | 1.71    | 1.71     | 1.71    |
| Expt.$^f$      |        |            |              |        |            |              | 2.3607941(4) | 364.684163(391) | 1.776085(189) | 408, 409.3 ± 8$^m$ |
| MgF            |        |            |              |        |            |              |
| CVDZ           | 1.7854 | 1.7782     | 1.7775       | 697.9  | 698.9      | 699.6        | 4.19    | 4.18     | 4.18    |
| CVTZ           | 1.7772 | 1.7627     | 1.7622       | 701.0  | 704.8      | 704.4        | 4.00    | 3.96     | 3.94    |
| CVQZ           | 1.7700 | 1.7541     | 1.7536       | 708.4  | 716.4      | 716.8        | 4.07    | 4.20     | 4.21    |
| CV5Z           | 1.7659 | 711.7      | 4.18          |        |            |              |        |            |        |
| Expt.$^g$      |        |            |              |        |            |              | 1.7499371(1) | 720.14042(30) | 4.26018(16) | 458, 458.5 ± 5.0$^m$ |
|        | \( r_e \) | \( \omega_e \) | \( \omega_e x_e \) | \( D_0 \) |
|--------|-----------|------------|-----------------|---------|
|        | Val RIV All | Val RIV All | Val RIV All | Val RIV All |
| MgCl   |           |            |                |          |
| CVDZ   | 2.2582 2.2558 2.2541 | 441.8 440.5 441.3 | 1.85 1.79 1.79 | 290.5 289.3 290.4 |
| CVTZ   | 2.2251 2.2137 2.2110 | 457.6 461.9 463.2 | 1.99 2.04 2.06 | 310.5 307.1 308.1 |
| CVQZ   | 2.2193 2.2053 2.2025 | 459.8 464.2 465.2 | 2.01 2.04 2.05 | 321.4 316.8 317.7 |
| Expt.   | 2.196(1) | 466.0(8) | 2.0(0) | 317, 324.5 ± 2.1\( ^m \) |
| KF     |           |            |                |          |
| CVDZ   | 2.2436 2.2514 2.2506 | 402.7 399.0 399.3 | 2.58 2.41 2.41 | 368.4 454.7 359.9 |
| CVTZ   | 2.1993 2.1980 2.1972 | 414.7 415.6 415.7 | 2.46 2.24 2.26 | 332.5 477.6 370.1 |
| CVQZ   | 2.1868 2.1800 2.1796 | 419.7 422.2 422.2 | 2.46 2.35 2.36 | 322.5 488.6 422.2 |
| CV5Z   |           |            |                |          |
| Expt.   | 2.1714559(2) | 426.261872(98) | 2.449801(44) | 489, 494 ± 2.5\( ^m \) |
| KCl    |           |            |                |          |
| CVDZ   | 2.9169 2.7709 2.7684 | 272.1 258.7 259.2 | 2.89 1.18 1.18 | 391.5 393.4 394.0 |
| CVTZ   | 2.9705 2.7045 2.7017 | 301.9 270.4 270.8 | 3.31 1.15 1.15 | 400.4 407.8 408.3 |
| CVQZ   | 2.9827 2.6829 2.6801 | 308.8 276.4 276.7 | 3.34 1.20 1.20 | 410.1 421.1 421.5 |
| CV5Z   |           |            |                |          |
| Expt.   | 2.666678(3) | 280.07639(490) | 1.31330(338) | 419, 428 ± 2.5\( ^m \) |
| CaF    |           |            |                |          |
| CVDZ   | 2.1269 2.0406 2.0399 | 405.4 536.4 536.3 | 30.03 2.62 2.62 | 342.7 473.3 432.8 |
| CV(D+3d)Z | 1.9902 | 571.3 | 3.00 | 508.5 |
| CVTZ   | 2.1125 1.9889 1.9880 | 399.2 562.3 563.0 | 38.60 2.75 2.78 | 310.5 508.4 399.4 |
| CV(T+2d)Z | 1.9692 | 574.3 | 2.85 | 532.3 |
| CVQZ   | 1.9981 1.9597 1.9595 | 537.6 583.6 583.5 | 5.37 2.87 2.87 | 361.0 531.1 463.9 |
| CV(Q+d)Z | 1.9585 | 584.1 | 2.88 | 531.6 |
| Expt.   | 1.9516403(1) | 588.644(2) | 2.91194(6) | 529, 524 ± 2.1\( ^m \) |
| CaCl   |           |            |                |          |
| CVDZ   | 2.6598 2.5770 2.5752 | 324.2 335.4 336.1 | 1.22 1.16 1.15 | 24.8 352.8 353.7 |
| CV(D+3d)Z | 2.5049 | 348.2 | 1.27 | 368.4 |
| CVTZ   | 2.5969 2.4921 2.4891 | 340.9 353.5 354.1 | 1.27 1.27 1.27 | 370.0 382.0 382.8 |
| CV(T+2d)Z | 2.4704 | 357.1 | 1.27 | 388.5 |
| CVQZ   | 2.5402 2.4531 2.4501 | 351.5 366.0 366.5 | 1.34 1.35 1.35 | 396.7 404.1 404.9 |
| CV(Q+d)Z | 2.4519 | 366.4 | 1.35 | 404.5 |
| Expt.   | 2.43674 | 370.201 | 1.3732 | 395, 406 ± 9\( ^m \) |

(a) (LiF) Hedderich, H.G., Engleman Jr., F.R., and Bernath, P.F., 1991, Can. J. Chem. 69, 1659.
(b) (LiCl) Burkholder, J.B., Hammer, P.D., Howard, C.J., Maki, A.G., Thompson, G., and Chackerian Jr., C., 1987, J. Mol. Spectrosc. 124, 139.
(c) (BeF) Tai, G. and Verma, R.D., 1995, J. Mol. Spectrosc. 173, 1.
(d) (BeCl) Huber and Herzberg.[57]
(e) (NaF) Muntianu, A., Guo, B., and Bernath, P.F., 1996, J. Mol. Spectrosc. 176, 274.
(f) (NaCl, KCl) Sam, R.S., Dulick, M., Guo, B., Zhang, K.-Q., and Bernath, P.F., 1997, J. Mol. Spectrosc. 183, 360.
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(h) (MgCl) Rostas, J., Shafizadeh, N., Taieb, G., and Bourguignon, B., 1990, Chem. Phys. 142, 97.
(i) (KF) Liu, M.-C., Muntianu, A., Zhang, K.-Q., Colarusso, P., and Bernath, P.F., 1996, J. Mol. Spectrosc. 180, 188.
(j) (CaF) Kaledin, L.A., Bloch, J.C., McCarthy, M.C., and Field, R.W., 1999, J. Mol. Spectrosc. 197, 289.
(k) (CaCl) Berg, L.-E., Bloch, J.C., McCarthy, M.C., and Field, R.W., 1999, J. Mol. Spectrosc. 197, 289.
(l) Single point energy calculation at experimental \( r_e \).
(m) All except last values from Huber and Herzberg.[57], last value from CRC Handbook corrected to 0 K with expt. \( \omega_e x_e \) and \( \omega_e \).
|            | \( r_e \) | \( \omega_e \) | \( \omega_e x_e \) | \( D_0 \) |
|------------|---------|---------|---------|---------|
|            | Val  | RIV    | All    | Val  | RIV    | All    | Val  | RIV    | All    |
| BeO        |      |        |        |       |        |        |       |        |        |
| CVDZ       | 1.3711 | 1.3674 | 1.3671 | 1366.3 | 1371.1 | 1372.0 | 11.47 | 11.22  | 11.18  |
| CVTZ       | 1.3456 | 1.3414 | 1.3407 | 1450.6 | 1457.1 | 1458.4 | 12.07 | 12.04  | 12.05  |
| CVQZ       | 1.3387 | 1.3334 | 1.3326 | 1470.7 | 1483.5 | 1484.2 | 12.07 | 12.11  | 12.12  |
| CV5Z       | 1.3373 | 1.3317 | 1.3308 | 1475.4 | 1488.2 | 1489.6 | 12.03 | 12.08  | 12.09  |
| Expt. \( ^a \) | 1.3309 |        |        | 1487.32 | 1366.3 | 1372.0 | 11.47 | 11.22  | 11.18  |
| BeS        |        |        |        |        |        |        |       |        |        |
| CVDZ       | 1.7764 | 1.7704 | 1.7722 | 960.2  | 966.2  | 964.8  | 5.74  | 5.81   | 5.81   |
| CVTZ       | 1.7607 | 1.7568 | 1.7551 | 977.5  | 982.6  | 983.7  | 5.82  | 5.83   | 5.86   |
| CVQZ       | 1.7519 | 1.7467 | 1.7443 | 990.9  | 996.6  | 998.3  | 5.87  | 5.88   | 5.90   |
| Expt. \( ^a \) | 1.7415(3) |        |        | 997.94 | 6.137  | (341) | 359.7 | 12.6d  |
| MgO        |        |        |        |        |        |        |       |        |        |
| CVDZ       | 2.1999 | 2.1952 | 2.1958 | 499.9  | 496.6  | 498.4  | 2.63  | 2.51   | 2.50   |
| CVTZ       | 2.1718 | 2.1600 | 2.1582 | 518.6  | 524.0  | 525.1  | 2.60  | 2.58   | 2.57   |
| CVQZ       | 2.1635 | 2.1491 | 2.1465 | 524.4  | 530.3  | 531.5  | 2.62  | 2.60   | 2.59   |
| Expt. \( ^b \) | 2.1425 |        |        | 528.74 | 2.704  | ≤ 232 | 231d  |        |
| MgS        |        |        |        |        |        |        |       |        |        |
| CVDZ       | 2.0360 | 2.0362 | 2.0531 | 777.5  | 779.9  | 490.2  | 2.17  | 2.25   | 2.15   |
| CV(D+d)Z   | 2.0395 |        |        | 557.1  | -10.94 |        |       |        |        |
| CV(D+2d)Z  | 1.9382 |        |        | 477.8  | 7.97   |        | 308.0 |        |
| CV(D+3d)Z  | 1.9095 |        |        | 565.5  | 11.78  |        | 318.8 |        |
| CVTZ       | 2.0206 | 1.9298 | 1.9284 | 824.3  | 523.1  | 525.7  | 31.47 | 3.37   | 3.74   |
| CV(T+d)Z   | 1.8540 |        |        | 661.2  | 8.71   |        | 360.5 |        |
| CV(T+2d)Z  | 1.8472 |        |        | 679.2  | 7.88   |        | 366.6 |        |
| CVQZ       | 2.0658 | 1.8308 | 1.8307 | 689.9  | 718.0  | 717.7  | 5.23  | 6.34   | 6.35   |
| CV(Q+d)Z   | 1.8281 |        |        | 722.2  | 6.13   |        | 393.3 |        |
| CV(Q+2d)Z  | 1.8274 |        |        | 723.3  | 6.11   |        | 393.9 |        |
| DK-CVQZ    | 1.8333 |        |        | 709.6  | 6.73   |        | 385.0 |        |
| DK-CV(Q+d)Z| 1.8305 |        |        | 714.1  | 6.54   |        | 387.5 |        |
| CV5Z       |        |        |        |        |        |        |       |        |        |
| Expt. \( ^c \) | 1.8222315(4) |        |        | 732.01377(40) | 4.81268(74) | ≥ 459 | 398.7 | 16.7d  |

(a) (BeO,BeS,MgS) Huber and Herzberg\[57\].
(b) (MgO) Mürtz, P., Thümmel, H., Pfelzer, C., and Urban, W., 1995, *Mol. Phys.* 86, 513.
(c) (CaO) Focsa, C., Poclet, A., Pinchemel, B., Le Roy, R.J., and Bernath, P.F., 2000, *J. Mol. Spectrosc.* 203, 330.
(d) First value from Huber and Herzberg\[57\], second from CRC Handbook\[55\] corrected to 0 K with \( \omega_x \) and \( \omega_e \).
(e) Single-point energy calculation at experimental \( r_e \). Results with the CV(5+d)Z and CV(5+2d)Z basis sets are 406.7 and 406.6 kJ/mol, respectively.
TABLE IX: Computed $^2D \leftarrow ^2S$ excitation energy (cm$^{-1}$) in Ca$^+$ as a function of the basis set.

| Basis Set                | D   | T   | Q   | 5   |
|-------------------------|-----|-----|-----|-----|
| CV(n+d)Z                | 38065 | 22546 | 13965 | 12374 |
| CV(n+2d)Z               | 28618 | 16539 | 12985 | 12898 |
| CV(n+3d)Z               | 21528 | 14920 | 12851 | 12885 |
| CV(Q+d)Z uncontracted   | 19214 | 15155 | —     | —     |
| DK-CV(Q+d)Z uncontracted| —    | —    | 13240 | —     |
| Best estimate$^a$       | —    | —    | 14201 | —     |

All calculations at the CAS-PT3 level with a [Ne] core frozen. The experimental values are $^2D_{3/2}$ 13650.19, $^2D_{5/2}$ 13710.88, spin-orbit averaged 13686.60 cm$^{-1}$.

(a) CV(5+2d)Z plus relativistic correction estimated as the difference between DK-CV(Q+d)Z and CV(Q+d)Z.