The accuracy of the pseudopotential approximation. I. An analysis of the spectroscopic constants for the electronic ground states of InCl and $InCl_3$ using various three valence electron pseudopotentials for indium

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Spectroscopic constants for InCl and $InCl_3$ are determined by a coupled cluster procedure using relatively large basis sets and an energy-consistent semilocal three valence electron pseudopotential for indium. Possible errors within the pseudopotential approximation are discussed in detail by comparison of available pseudopotentials adjusted through different techniques. Core-polarization corrections and the deviation from a point core approximation are discussed. These corrections, however, do not lead to more accurate bond distances as compared to the experimental results. Differently adjusted three valence electron pseudopotentials yield quite different results for the bond distances of InCl and $InCl_3$. The single-electron adjusted energy-consistent pseudopotential of Igel-Mann *et al.* [Mol. Phys. **65**, 1321 (1988)] yields the best results and therefore, this pseudopotential has been chosen for all further investigations on molecular properties. The Dunham parameters for InCl are calculated by solving the vibrational-rotational Schrödinger equation numerically. A finite field technique is used to determine the dipole moment and dipole-polarizability of diatomic InCl. The dependence of several molecular properties on the vibrational quantum state is determined by calculating the expectation value $P_n=\langle n|P(R)|n\rangle$, where $P(R)$ is the distance dependent molecular property. The $P(R)$ curves show strong linear behavior and therefore, the shape of the P_n curve is mostly determined by anharmonicity effects in the InCl potential curve. For the vibrational ground state, $|0\rangle$, the calculated property P_0 deviates only slightly from the property determined directly at the equilibrium distance, P_e. There is in general satisfying agreement of our calculated values with available experimental results. However, it is concluded that in order to obtain very accurate spectroscopic constants a small core definition for indium has to be preferred. © *1995 American Institute of Physics.*

INTRODUCTION

For heavy element containing compounds relativistic effects become important and cannot be neglected.[1] The scalar relativistic pseudopotential method is the most widely used approximation to account for such effects and recently, spin–orbit coupled pseudopotentials have been developed for most of the heavy elements.[2] However, the pseudopotential approximation[3–5] has openly been criticized.[6–8] Both Malli and Pyper stated that relativistic pseudopotential schemes are theoretically dubious and that the reliability of such calculations is always open to question until these have been checked against accurate all-electron calculations.[6,7] All current (nonrelativistic and relativistic) model potential schemes start from the (generalized) Phillips–Kleinman (PK) operator.[3,4] The main difficulties arise when the PK operator is replaced by some pseudo-operators leading either to *ab initio* model potentials (AIMP) (Ref. 9) or to the more common pseudopotentials having nodeless valence orbitals for the lowest symmetry states (abbreviated simply as PP, pseudopotentials, or ECP, effective core potentials). We mention that four component relativistic pseudopotential procedures using nodeless valence orbitals[10] lack indeed some justification on how one should treat the pseudo-operator acting on the small component ϕ_s, since ϕ_s has most of its density below the usual cutoff region of the large component ϕ_L.

For the widely used scalar relativistic or spin–orbit coupled pseudopotentials one faces two major points of criticism. First, relativistic perturbation operators[11] usually act in close vicinity of the nucleus and nodeless orbitals used in most pseudopotential approximations (PPA) have the wrong functional behavior in such regions. This criticism may, however, only be partly justified since relativistic effects are "shifted" into the valence region within the pseudopotential approximation.[7,12] Even more convincingly, benchmark cal-

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culations on relativistic effects show very encouraging results when comparing to other techniques.[13] The second criticism is that different pseudopotential parameters published yield quite different results for molecular properties[8,14] and titles such as "*Pseudopotentials that work*"[15] may lead to the opinion that some of the published pseudopotentials work and some not. Moreover, one may obtain results of different quality for different molecules. Therefore, an interesting debate on the *transferability* of pseudopotentials, i.e., the validity of this approximation for the calculation of molecular properties, has arisen in the last few years, see for example the various discussions and replies in Refs. 8, 14, 16, and 17. *It is of great interest whether or not pseudopotentials are able to produce accurate spectroscopic constants comparable to Hartree–Fock and experimental results*. We will therefore discuss some aspects of the pseudopotential approximation in detail.

In this first paper of our series we study different three valence electron pseudopotentials for indium. It turns out that effects usually neglected in pseudopotential schemes can be unusually large for the bond distance of diatomic InCl. We mention that the Cl$(3s)$ valence orbital is quasidegenerate with the In$(4d)$ core orbital[18] and therefore, diatomic InCl is an interesting test case for various pseudopotential definitions.

In a previous paper we showed that the decomposition of group 13 compounds $MX_3 \rightarrow MX + X_2$ (X=H,F) is not very dependent upon electron correlation.[19,20] Hence, even at the Hartree–Fock level one can obtain reasonable decomposition energies.[20] This is in contrast, for example, to the decomposition of Au(III) compounds, $AuX_4^- \rightarrow AuX_2^- + X_2$, which is very sensitive to electron correlation effects.[21] Raghavachari and Trucks highlighted the difficulties inherent in the Møller–Plesset (MP) theory for transition elements.[22] In a recent paper we investigated the convergence of the many body perturbation theory for molecular properties of group 13 compounds in some detail. It is of interest whether a method most intensively used in quantum chemistry such as MP2 can accurately predict dissociation energies for main group compounds.[22]

Barett and Mandel reported accurate spectroscopic constants determined from the microwave spectrum of InCl.[23] Only InCl has been studied theoretically by other groups.[24–26] Von Niessen investigated the ionization potential of InCl using Green's function methods.[26] Dobbs and Hehre carried out all-electron calculations using a 3-21G* basis set obtaining quite reasonable results for the bond distance and dipole moment of InCl.[25] Balasubramanian *et al.*[24] used Hay–Wadt pseudopotentials[27,28] with a rather limited basis set. They obtained a dipole moment for InCl which is 0.8 D below the experimental value. They contributed part of this effect as to be due to the difference between the dipole moment at the equilibrium distance, μ_e, and the vibrationally averaged dipole moment for the vibrational ground state $(n=0)$ of InCl, $\mu(0)$. However, this would be an unusually large vibrational effect not reported so far for any molecule and we will investigate vibrational contributions to molecular properties in detail. There is also some uncertainty about the vibrational behavior of the chlorine nuclear quadrupole coupling constant (NQCC). Delvigne and Wijn obtained for the ^{35}Cl NQCC $(-13.71+0.4n)$ MHz (n =vibrational quantum number),[29] while Hoeft *et al.* measured $(-13.63-0.6n)$ MHz with the opposite sign.[30] In both cases the experimental uncertainty is quite large.[29,30]

This paper contains essentially two independent parts. We first discuss the pseudopotential approximation in detail. Since the coupled cluster calculations[31] performed for $InCl_3$ become quite demanding in computer time, we decided to use a "less accurate" three valence electron pseudopotential for all future investigations, and show that even such an approximation can lead to reliable molecular properties in good agreement with experimental results. Pseudopotential calculations using a smaller core definition will be presented in a subsequent paper. We present Møller–Plesset[32] and coupled cluster calculations[31] to determine a variety of spectroscopic constants of InCl and $InCl_3$. Some of these, like the polarizability of InCl and the decomposition energy of $InCl_3$, are not known experimentally. We also study ^{35}Cl^{37}Cl isotope effects because experimental data for comparison are scarce.

COMPUTATIONAL DETAILS

To start we chose an energy adjusted semilocal 3-valence electron pseudopotential (PP) of Igel-Mann *et al.*, obtained by a single-electron fit procedure (SEFIT) (Ref. 33) to produce molecular properties for InCl and $InCl_3$. The molecular valence Hamiltonian used is defined as follows (in a.u.):[34]

$$H=-\frac{1}{2}\sum_i \Delta_i+\sum_{i<j}\frac{1}{r_{ij}}+\sum_{\lambda<\mu}\frac{Q_\lambda Q_\mu}{R_{\lambda\mu}}+\sum_{i,\lambda} V_\lambda^P(r_{i\lambda}) \tag{1}$$

with a semilocal pseudopotential for core λ,

$$\begin{aligned} V_\lambda^P(r_{i\lambda}) &= -\frac{Q_\lambda}{r_{i\lambda}}+\sum_l P_{\lambda l}\sum_k A_{\lambda lk}e^{-a_{\lambda lk}r_{i\lambda}^2} \\ &= -\frac{Q_\lambda}{r_{i\lambda}}+\sum_l V_{\lambda l}(r_{i\lambda}), \end{aligned} \tag{2}$$

i and j are electron indices, λ and μ are core indices, Q_λ is the charge of core λ $(Q_{\mathrm{In}}=3,\ Q_{\mathrm{Cl}}=17)$ and $P_{\lambda l}$ is the projection operator onto the Hilbert subspace of core λ with angular symmetry l. The parameters $A_{\lambda lk}$ and $a_{\lambda lk}$ are adjusted to the important valence spectrum of the corresponding atom. In contrast to other fit procedures (shape consistent PP, norm-conserving PP) (Refs. 35,36) we like to introduce the term *energy-consistent* PP for our fit technique. Energy-consistent PPs produce nodeless pseudo-orbitals for the lowest valence states.

The experimental energies of indium for the SEFIT procedure were taken from Refs. 37 and 38. We will see later on that this SEFIT PP (Ref. 33) produces very good results for the bond distances of InCl and $InCl_3$ when compared to other fit techniques and therefore, we use the simple SEFIT PP for all calculations on spectroscopic constants of InCl and $InCl_3$. The basis set for indium was an uncontracted $(7s/6p/1d)$

valence set as described in Ref. 39. Chlorine is treated as an all-electron atom in all calculations in order to avoid additional errors resulting from a pseudopotential approximation for the chlorine atom. For chlorine we used a Dunning $(13s/10p/1d)/(8s/6p/1d)$ set[41] which includes one diffuse s-function with exponent 0.059, one diffuse p-function with exponent 0.034 and one d-polarization function with exponent 0.56. For $InCl_3$ this leads to 174 Gaussian functions contracted to 123 basis functions. The Møller–Plesset[32] and quadratic configuration interaction [QCISD(T)] (Ref. 31) procedures within the GAUSSIAN92 program series were used.[42] 37 points for the potential curve of InCl and 10 points for $InCl^+$ were determined. For InCl the first 20 vibrational and 20 rotational level (per vibronic state) were taken into account for solving the vibrational-rotational Schrödinger-equation numerically.[43] The Dunham fit was used to obtain spectroscopic constants from the calculated vibrational-rotational spectrum of InCl.[44] The sign definition of Huber and Herzberg was used for the Dunham series.[45] Spectroscopic constants smaller than 10^{-8} cm^{-1} are neglected in this analysis. For $InCl_3$ we calculated the harmonic vibrational spectrum only up to the MP3 level[42,46] because the frequencies seem not to be very dependent upon electron correlation. The isotopes ^{115}In, ^{35}Cl, and ^{37}Cl were used for the vibrational analysis. Isotope effects resulting from ^{113}In are comparably small and were therefore neglected (compare the reduced masses in g/mol for ^{113}In^{35}Cl: 26.5066, ^{115}In^{35}Cl: 26.6161, ^{115}In^{37}Cl: 27.7662). The dipole moment μ and the static dipole polarizability α were determined by using the finite field technique (FFT) with small electric fields of ± 0.002 a.u. in parallel direction to the molecular axis and of $+0.002$ a.u. in perpendicular direction to the molecular axis. The internuclear distance dependence of the dipole moment and dipole-polarizability was determined for a small distance range around the equilibrium bond length. The dependence of the averaged internuclear distance R, the dipole moment, the static dipole polarizability and the electric field gradient on the vibrational structure of the molecule has been determined by calculating the matrix elements $\langle n|P|n\rangle$ (abbreviated as P_n in the following) for a particular vibronic state $|n\rangle$ and molecular property P.[47] Since the rotational dependence was found to be insignificant, we set $J=0$, use the abbreviation $|n\rangle \equiv |n,J=0\rangle$ and all P_n values reported are averaged over the rotational ground state $J=0$. We used the formula e^2qQ/h (MHz)$=234.9$ (eq/a.u.) ($eQ/10^{-24}$ cm^2) to convert field gradients given in a.u. to nuclear quadrupole coupling constants (NQCC) in MHz. The nuclear quadrupole moments of Ref. 48 were used, $-0.081\,65$ $eQ/10^{-2}$ cm^2 for ^{35}Cl and $-0.064\,35$ $eQ/10^{-2}$ cm^2 for ^{37}Cl.

ACCURACY OF THE PSEUDOPOTENTIAL APPROXIMATION

If ‘‘accurate’’ spectroscopic constants from *ab initio* calculations are reported one should discuss possible errors in the computational procedure. Beside basis set effects like basis set superposition and extension errors, which are small at the HF and CI level for the basis sets used here, the main source of error lies in the pseudopotential approximation (PPA).[49] Well known error sources within the PPA using nodeless orbitals are,

(i) the nonconstancy of the atomic core with increasing number of valence electrons and the molecular field;
(ii) errors resulting from the pseudoorbital transformation and the fit procedure, the pseudopotential ansatz itself, defects in the basis set used in the fit procedure etc.;
(iii) core-overlap effects;
(iv) core-polarization effects; and
(v) the possible overestimation of valence correlation effects due to the inner nodeless behaviour of the valence orbitals.

All these effects are usually assumed to be rather small if the core has been carefully chosen, the fit-procedure has been carried out with great care and basis sets of high quality are applied. One should avoid a large number of fit functions (normally Gaussian functions) in order to avoid unphysical oscillations in the PP and one has to take care, that higher angular quantum states in the pseudoatom are well described, for instance by a local potential, or by a semilocal potential including higher l-terms in the projection operator since they become important at larger distances. The latter effect (v) may be more difficult to avoid, see for example the discussion of Pittel and Schwarz[50] and Teichteil *et al.*[51] The two corrections (iii) and (iv) are rather difficult to account for, especially for large and polarizable cores. Effect (i) can be partially compensated by using energy-consistent PPs determined by a multielectron fit procedure (MEFIT) instead of a single one valence electron fit procedure (SEFIT),[52] in other words, one should adjust to a rather extensive valence spectrum of the atom and ions including the important spectrum of the neutral atom, as emphasized very early by Durand and Barthelat.[53] We like to point out that the adjustment of the PP parameters has little to do with the basis set determined for a certain PP. The pseudopotential parameters are usually determined from numerical all-electron calculations, which are independent of any basis set. This is in contrast to *ab initio* model potentials used by Huzinaga and co-workers.[9] Like in the *ab initio* all-electron case, the basis set is adjusted after the parameters have been determined, usually by an energy minimization procedure. Hence, to compare the performance of different PPs one should use the same quality in the basis set expansion (see discussion in Ref. 14).

In order to test the reliability of the simple three valence electron SEFIT PP for indium, additional HF and MP2 calculations for InCl and $InCl_3$ using the MEFIT PP of Bergner *et al.*[54] (MEFIT1) were carried out, Table I. The MEFIT1 PP leads to ~0.03 Å shorter bond distances (MEFIT1$+V_{l=3}$, Table I) compared to the SEFIT PP. The original SEFIT PP does not contain a term for the higher angular quantum number $l=3$ $(V_{l=3}=0)$ (Ref. 33) in contrast to the MEFIT1 PP. It is therefore of interest to test the importance of higher angular momentum contributions to the PP. The values listed in Table I show that part of the decrease in the bond distance when changing from the SEFIT to the MEFIT1 PP is indeed due to the $V_{l=3}$ term, i.e., compare the MEFIT1$+V_{l=3}$ with the MEFIT1 results. The MP2 results show a similar picture.

TABLE I. Bond distances (in Å) for $^1\Sigma^+$ InCl using various three valence electron PPs.[a]

	InCl		$InCl_3$	
	HF	MP2	HF	MP2
Expt		2.401		2.28±0.01
SEFIT	2.422	2.411	2.284	2.292
SEFIT+CPP	2.383	2.376	2.249	2.261
SEFIT+CPP+CRC	2.384	2.377	2.251	2.263
MEFIT1	2.405	2.395	2.279	2.284
MEFIT1+$V_{l=3}$	2.391	2.381	2.266	2.272
MEFIT1+$V_{l=3}$+CPP	2.350	2.346	2.233	2.244
MEFIT1+$V_{l=3}$+CPP+CRC	2.352	2.347	2.234	2.245
MEFIT2	2.414	2.404	2.282	2.289
MEFIT2+$V_{l=3}$	2.401	2.391	2.270	2.276
MEFIT2+$V_{l=3}$+$V_{l>3}$	2.393	2.383	2.262	2.268
CE	2.432	2.420	2.290	2.297
CE+$V_{l=3}$	2.411	2.401	2.273	2.280
CE+$V_{l>2}$	2.380	2.368	2.238	2.244
T	2.428	2.418	2.293	2.299
HW	2.439	2.426	2.296	2.303
HW+$V_{l=3}$	2.423	2.411	2.283	2.290
HW+$V_{l>2}$	2.401	2.390	2.263	2.269

[a] SEFIT, single electron fit PP; MEFIT, multi electron fit PP; CE, averaged relativistic PP from Christiansen-Ermler *et al.* (Ref. 55). T, Toulouse PP (Ref. 40); HW: Hay–Wadt PP (Refs. 27 and 28); CPP, core-polarization potential; CRC, core-repulsion correction (Fig. 1). If not otherwise stated, all PPs contain only the nonlocal operators up to $l=2$. Experimental values from Refs. 45 and 56–58.

For the core-polarization (CP) (Ref. 59) we use the formalism introduced by Müller, Flesch, and Meyer[60] (see also Schwarz *et al.*[61]) and consequently applied to the pseudopotential approximation by Stoll, Szentpaly, and co-workers,[62,63]

$$V_{\mathrm{pol}}=-\frac{1}{2}\sum_{\lambda}\alpha_\lambda f_\lambda^2. \tag{3}$$

V_{Pol} is the core-polarization potential (CPP), α_λ is the dipole polarizability of the core λ (In^{3+} in our case), and $\mathbf{f}_\lambda$ is the vector field produced by the valence electrons and the other nuclei at core λ,

$$\mathbf{f}_\lambda=\sum_i \frac{\mathbf{r}_{ij}}{r_{ij}^3}(1-e^{-\delta_\lambda r_{\lambda i}^2})^q-\sum_{\mu\neq\lambda} Q_\mu \frac{\mathbf{r}_{\lambda\mu}}{r_{\lambda\mu}^3} \times(1-e^{-\delta_\lambda r_{\lambda\mu}^2})^q. \tag{4}$$

We chose $q=1$, α=3.22 a.u. for In^{3+} and a cutoff parameter of δ=0.3535.[33] Only first order effects in the multipole expansion are considered, i.e., we neclect quadrupole and higher multipole effects. The corresponding multicenter integrals over Cartesian Gaussian functions are solved[64] and have recently been brought into an efficient computer code.[65] The HF results including the CPP are listed in Table I.

Core-polarization effects decrease the bond distance by 0.03–0.04 Å for InCl and $InCl_3$. The final MP2 MEFIT1 +CPP bond distance of 2.346 Å for InCl (exp.2.401 Å) (Ref. 45) and 2.244 Å for $InCl_3$ (exp. 2.28±0.01 Å) (Refs. 56–58) are now much below the experimental values. The MP2 calculations on InCl show that valence correlation diminishes the bond distance by ~0.01 Å, hence the final calculated bond distance of InCl is ~0.06 Å below the experimental value. For $InCl_3$ valence correlation slightly *increases* the bond distance by ~0.005–0.008 Å. The experimentally determined bond distance of $InCl_3$ ($r_a=2.289$ Å (Ref. 57) may be slightly larger compared to the r_e value since it originates from a gas phase electron diffraction study at 315 °C (a typical correction for this effect is ~0.01 Å, see discussion below). Hence, the corrected experimental bond distance will be in rather good agreement with our calculated value of 2.272 Å, but without inclusion of a CPP (in contrast to diatomic InCl). However, if a CPP is included the bond distance is ~0.04 Å below the experimental value.

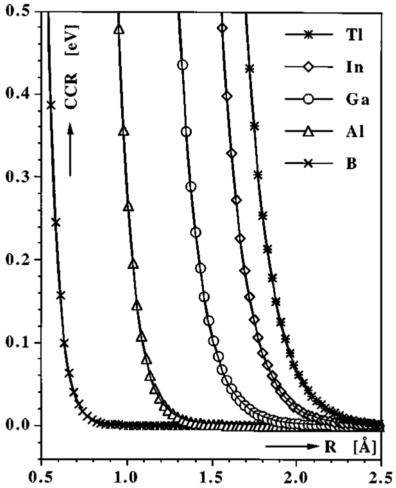

FIG. 1. Core–core repulsion correction (CCR) for the group 13 monofluorides.

We also tested a different cutoff function using $q=2$. From a Taylor expansion of the cutoff function one can estimate that the new exponent δ' for $q=2$ is related to the old exponent δ for $q=1$ by $\delta'>\delta$ for small δ, and a fit-procedure as described in Ref. 33 yields δ'=0.619. For InCl this gives a bond distance of 2.348 Å at the HF level using the MEFIT1 PP+CPP similar to the previous value of 2.350 Å for $q=1$. A multireference CISD calculation with 49 728 contracted and 1 222 572 uncontracted configurations using this pseudopotential gives 2.346 Å, hence MP2 overestimates the effect of valence-correlation on the InCl bond distance.

The dissociation energy is less sensitive to correlation effects, the CPP correction increases D^0 from 3.621 to 3.703 eV (without zero-point vibrational correction). The harmonic frequency (force constant) increases from 298.9 cm^{-1} (1.411

TABLE II. Fit parameters for the core–core repulsion correction (CCR) of the group 13 chlorides.[a]

	BCl	AlCl	GaCl	InCl	TlCl
A	8.9635	42.2972	32.4532	79.6647	99.3890
a	3.8554	2.5601	1.8054	1.6530	1.5492

[a] $V_{\mathrm{CCR}}(R)=17A\times10^{-aR}$. All values in a.u.

TABLE III. MEFIT2 pseudopotential.[a]

l	k	A	α
s	2	28.964 450 98	1.460 343 79
		−4.059 875 13	0.710 037 03
p	2	36.977 213 71	1.535 023 65
		−3.346 654 73	0.781 018 25
d	2	4.498 156 61	0.600 597 34
f	1	−6.019 109 52	0.884 187 65
g	1	−6.019 088 14	0.884 469 38

[a] l, angular quantum number; k, number of Gaussians [see Eq. (2)].

mdyn/Å) to 301.8 cm^{-1} (1.438 mdyn/Å) due to inclusion of CPP.

As mentioned above, core-overlap effects may also be important.[66,67] In order to estimate the deviation from a point-charged core model introduced by the pseudopotential approximation we write down the Coulomb interaction between a point charge Q_A (in our case the chlorine nucleus, i.e., $Q_{\mathrm{Cl}}=17$) and a core B with the density distribution ρ_B,

$$V(\mathbf{r}_A,\mathbf{r}_B)=\int \frac{\rho_B(\mathbf{r}-\mathbf{r}_B)Q_A\delta(\mathbf{r}'-\mathbf{r}_A)}{|\mathbf{r}-\mathbf{r}'|}\,d(\mathbf{r},\mathbf{r}'). \tag{5}$$

From this we obtain an estimate for the nucleus–core repulsion correction V_{CCR},

$$V_{\mathrm{CCR}}=-Q_A\sum_{r\in \mathrm{core}} J_r+\frac{Q_A(Z_B-Q_B)}{r_{AB}}. \tag{6}$$

The Coulomb contributions J_r from the core B were calculated at the nonrelativistic and relativistic level using a modified version of the numerical Dirac–Fock program MCDF81.[68] Figure 1 shows the calculated core–core repulsion corrections V_{CCR} for a 3-valence electron system and one chlorine atom for the atoms B, Al, Ga, In, and Tl. Table II contains an exponential fit to these curves. For InCl_3 we assume the relation $V_{\mathrm{CCR}}(\mathrm{InCl}_3)=3\cdot V_{\mathrm{CCR}}(\mathrm{InCl})$. Table I shows that CCR effects are rather small for InCl and InCl_3 and may be neglected. This can be understood since the bond distances of InCl and InCl_3 are in a region where the CCR is still small, Fig. 1. It may be interesting to list the CCR (from Table II) at the bond distance[45] of the particular group 13 chloride BCl 1.516 Å (8.2×10^{-10} eV), AlCl 2.130 Å (6.1×10^{-7} eV), GaCl 2.202 Å (2.9×10^{-4} eV), InCl 2.401 Å (1.2×10^{-3} eV), TlCl 2.485 Å (2.4×10^{-3} eV). As can be seen the CCR corrections are very small for all group 13 chlorides and even CCR taken from the neutral indium atom instead of In^{3+}, which will have a larger core and therefore a larger CCR correction, does not change this situation.

In order to estimate possible errors in the fit procedure we repeated the MEFIT technique using 31 different valence states from all-electron Wood–Boring[69] calculations. This fit-procedure includes the one valence electron states originally used for the SEFIT procedure. In Table III we list the newly adjusted PP parameters and Table IV compares the HF valence spectrum produced by the different PPs. As can be seen the MEFIT2 PP describes most accurately the valence spectrum of the indium atom. The MEFIT2 bond distance now lies in between the SEFIT and MEFIT1 results for both InCl and InCl_3. However, the inclusion of CPP and higher angular momentum terms would still lead to a bond distance of ∼0.05 Å too short compared to the experimental value.

TABLE IV. Valence spectrum of indium using various PPs.[a]

	AE	SEFIT	MEFIT1	MEFIT2	HW	T	CE
$5s^2 5p^1$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
$5s^1 5p^2$	4.9821	4.9089	5.0141	4.9459	4.8521	5.0232	5.0059
$5s^2$	5.1259	5.1307	5.1012	5.1283	5.0776	5.0979	5.1246
$5s^1 5p^1$	10.2296	10.1481	10.2422	10.1834	10.0454	10.2675	10.2550
$5p^3$	11.7527	11.6878	11.8966	11.7500	11.5749	11.9519	11.8967
$5p^2$	17.1645	17.0910	17.3026	17.1503	16.9398	17.3896	17.3229
$5s^1$	22.1515	22.1123	22.0951	22.0967	21.9369	22.2442	22.2359
$5p^1$	29.1743	29.1431	29.2652	29.1498	28.9321	29.4911	29.4109
$6s^1$	36.8120	36.8467	36.8407	36.8157	36.5219	37.1695	37.0816
$5d^1$	36.9878	37.0744	36.9889	36.9699	36.7969	37.6473	37.4396
$6p^1$	39.0454	39.0847	39.1044	39.0320	38.7969	39.4465	39.3800
$4f^1$	40.9707	41.2153	40.9571	40.9529	40.7992	41.6674	41.3785
$7s^1$	41.8706	41.9473	41.8824	41.8672	41.6435	42.3420	42.2235
$6d^1$	42.0064	42.0973	42.0283	41.9892	41.8222	42.6227	42.4283
$7p^1$	42.8878	42.9649	42.9167	42.8764	42.7342	43.3503	43.2698
$5f^1$	43.7498	43.9704	43.7360	43.7318	43.5787	44.4225	44.1617
$5g^1$	43.8573	43.9704	43.8446	43.8392	43.7031	44.4225	44.2963
$8s^1$	44.2689	44.3620	44.2702	44.2598	44.1153	44.7840	44.6596
$7d^1$	44.3522	44.4494	44.3648	44.3344	44.1782	44.9459	44.7770
$8p^1$	44.8179	44.9108	44.8300	44.8050	44.6316	45.3184	45.2234
$6f^1$	45.2781	45.4670	45.2646	45.2604	45.1111	45.9191	45.6975
$6g^1$	45.3539	45.4670	45.3412	45.3358	45.1997	45.9191	45.7929
$9s^1$	45.5988	45.6995	45.5944	45.5810	45.4192	46.1339	46.0085
$8d^1$	45.6516	45.7534	45.6559	45.6335	45.4843	46.2338	46.0807
$9p^1$	45.9286	46.0290	45.9314	45.9142	45.7541	46.4511	46.3466

[a] All energies are in eV and are obtained from numerical calculations including the Wood–Boring operator (Ref. 69) in the all-electron case (AE). The total energy of ($5s^2 5p^1$) ground state is set to zero.

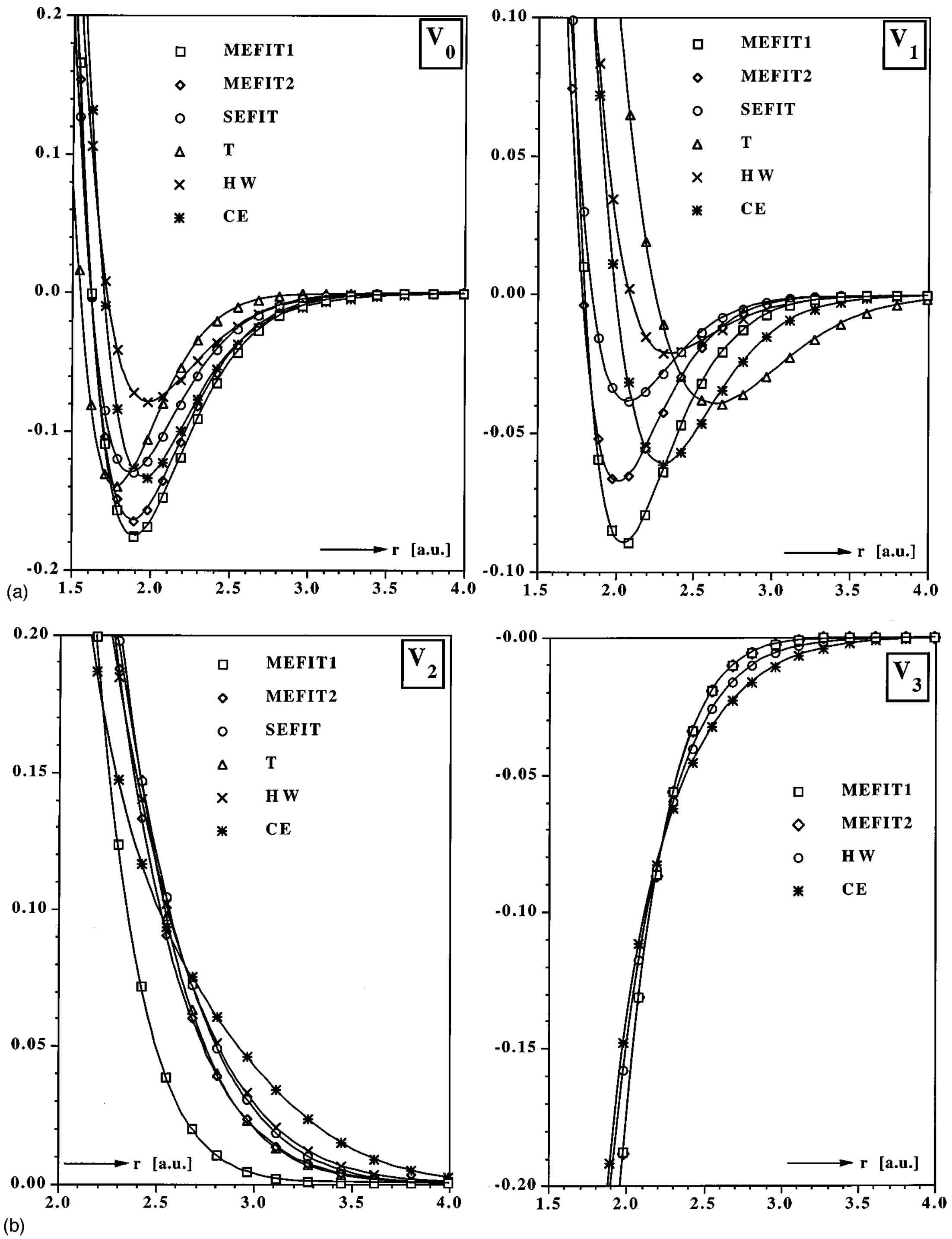

FIG. 2. Comparison of various 3-valence electron PPs for $l = 0$, 1, 2, and 3 (in a.u.).

This clearly shows that a three valence electron energy-consistent multielectron adjusted PP including CPP and CRC corrections *cannot* accurately reproduce the bond distance of InCl! It is therefore interesting to compare with other fit techniques used by other groups.

Table I shows a comparison of all current three valence electron pseudopotentials of indium for the molecules InCl and $InCl_3$. Note that the bond lengths of the different PPs in use vary from 2.428 Å (T) to 2.380 Å (CE+$V_{l>2}$), hence the variation of the InCl bond distance by different PP approximations is ~0.05 Å! A similar situation is found for $InCl_3$. However, if one compares the pseudopotentials leaving out the $V_{l>2}$ projectors, the variation is only 0.027 Å at the HF level. Figure 2 compares the functional form of the different pseudopotentials for indium. In order to show the differences between the curves more clearly, we leave out the centrifugal term and the core-electron Coulomb attraction in the potential and show the Gaussian expansion only, V_l [Eq. (2)]. Figure 2 clearly demonstrates that the different fitting schemes in use lead to quite different functional forms of the

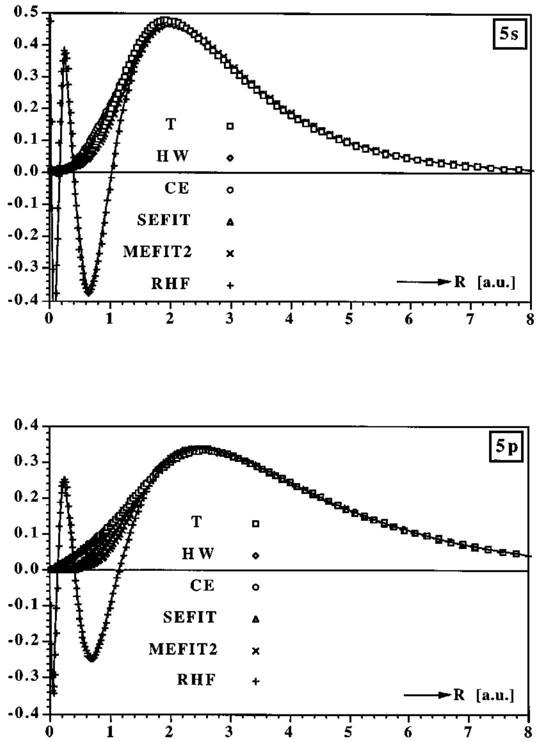

FIG. 3. Orbital plots for the ground state of indium using various pseudopotential approximation (see text). RHF, all-electron Wood–Boring calculations.

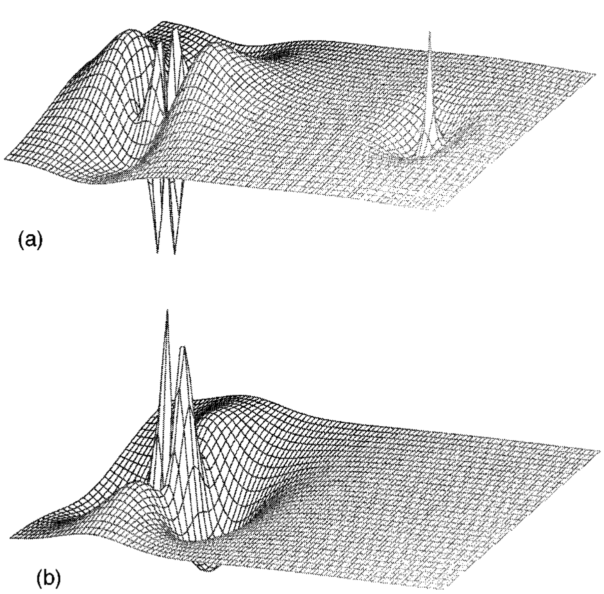

FIG. 4. InCl occupied In($4d$) σ-MO with Cl($3s$) admixture. (a) Canonical MO. (b) Localized MO.

pseudopotentials. The shape-consistent PPs are more repulsive in the $l=1$ term (V_l in Fig. 2) compared to the energy-consistent PPs, and this explains the larger bond distances for the HW, CE, and T PPs compared to the SEFIT, MEFIT1, and MEFIT2 PPs (if $V_{l>2}=0$). Table IV shows, however, that the shape-consistent pseudopotentials deviate quite substantially from the all-electron HF valence spectrum of indium.

Figure 3 shows the $5s$ and $5p$ orbitals of ground state indium ($5s^2 5p^1, {}^2P$) derived numerically[69] from various PPs in comparison with all-electron Wood–Boring results. Despite the large deviations between the different PP functions (Fig. 2), there is very good agreement between the different models used. This again points out that shape-consistency for some few chosen orbitals is *not* a guarantee for the overall quality of the pseudopotential approximation. We point out, however, that the energy-consistent PPs seem to satisfy shape-consistency automatically.

A comparison between the nf^1 and ng^1 valence energies shows only slight energy differences, for example, the $5f^1$ and $5g^1$ levels are almost degenerate and even $V_{l=3}=0$ produces good results, Table IV. In other words, $5f$ and $5g$ in indium behave almost hydrogen like (with $Z=3$). Hence, one may conclude that the f-operator can be neglected (as in the case of the SEFIT PP) or at least treated locally for $l>2$ [as in the case of the CE PP (Ref. 55)]. It is therefore even more surprising that the f-part of the PP has such a large influence on the InCl bond distance (Table I). Moreover, if the $V_{l>3}$ term is included in the MEFIT2 PP ($l=4$ term in Table III) the bond distance changes substantially, i.e., inclusion of this term lowers the InCl bond length by 0.008 Å. Similar large effects of such higher angular momentum terms are found for the HW and CE PPs as well, Table I. We note that in an earlier study on CaO by Igel-Mann *et al.* using a 2-valence electron PP for Ca similar strong dependencies of the intermolecular distance on higher l-terms have been found.[70]

We mentioned at the beginning that the Cl($3s$) orbital is quasidegenerate with the In($4d$) orbital[18] and therefore, the indium $4d$-orbital can directly influence the Cl(s) participation in the In–Cl bond. The HF canonical orbitals show indeed a large mixing in the responsible occupied σ-MO, as this is shown in Fig. 4(a). However, after a Boys localization procedure this orbital becomes decoupled from Cl($3s$), Fig. 4(b). Furthermore, a Mulliken population analysis at the HF or MP2 level shows a fully occupied d-core ($n_{4d}=10.29$ at the HF level). It is not clear, therefore, whether the deviation of our results from the experimental values is really due to In($4d$)–Cl($3s$) mixing.

Finally, errors in the relativistic treatment cannot be responsible for the small calculated bond distance of InCl, preliminary all-electron HF results show that the bond distance of InCl slightly *increases* from 2.448 to 2.453 Å due to relativistic effects. We also believe that the different relativistic schemes used in the fit procedure are not responsible for the relatively large differences in the functional forms of the various PPs. This is supported by the fact that for the $5p$ state, which shows smaller scalar relativistic effects compared to the $5s$ state, we obtain the largest deviations in the functional behavior, Fig. 2.

A more detailed study of all group 13 halides will be necessary in order to analyze the validity of a large core definition having only three electrons in the valence space. It is questionable if such an approximation for the group 13 elements is sufficient regarding the result of our calculations

TABLE V. Spectroscopic constants for the $^1\Sigma^+$ ground states of InCl using the SEFIT PP.[a]

	HF	MP2	MP3	MP4SDQ	QCISD	QCISD(T)	Expt.
R_e	2.422	2.411	2.410	2.412	2.413	2.414	2.401
D_0^0	3.417	4.460	4.277	4.219	4.207	4.287	4.44
IP_v	8.59	9.19	9.26	9.26	9.25	9.23	9.75[b]
$\mathrm{IP}_{\mathrm{ad}}$	8.48	9.05	9.17	9.19	9.19	9.17	9.51[b]; 9.60 ± 0.08[c]
In(115)Cl(35)							
ω_e	298.8	308.0	308.7	307.1	306.3	306.2	317.4
$\omega_e x_e$	0.970	0.908	0.906	0.908	0.915	0.901	1.032
$\omega_e y_e$	1.29	0.97	0.97	0.98	0.99	0.96	
B_e	0.1072	0.1082	0.1083	0.1081	0.1080	0.1079	0.1091
α_e	0.520	0.493	0.493	0.495	0.497	0.493	0.518
D_e	5.55	5.33	5.32	5.34	5.36	5.35	5.14
γ_e	0.77	0.74	0.75	0.76	0.75	0.75	0.84
μ_e	−3.887	−3.615	−3.656	−3.630	−3.618	−3.520	−3.79
$\alpha_\parallel$	68.74	73.07	71.30	72.00	72.48	73.99	
$\alpha_\perp$	47.50	46.03	45.18	45.06	45.11	45.19	
$\langle R\rangle$	2.426	2.415	2.414	2.416	2.417	2.418	
$\langle\mu\rangle$	−3.922	−3.646	−3.687	−3.660	−3.648	−3.549	
$\langle\alpha_\parallel\rangle$	68.86	73.23	71.45	72.18	72.66	74.21	
$\langle\alpha_\perp\rangle$	47.48	46.02	45.16	45.05	45.09	45.18	
In(115)Cl(37)							
ω_e	292.6	301.6	302.2	300.7	299.8	299.8	311.3
$\omega_e x_e$	0.930	0.870	0.869	0.870	0.877	0.864	0.993
$\omega_e y_e$	1.21	0.91	0.91	0.92	0.93	0.89	
B_e	0.1028	0.1037	0.1038	0.1036	0.1035	0.1034	
α_e	0.488	0.463	0.463	0.464	0.467	0.463	
D_e	5.07	4.90	4.89	4.91	4.92	4.92	
γ_e	0.72	0.68	0.70	0.70	0.69	0.69	
InCl^+							
R_e	2.265	2.259	2.274	2.283	2.270	2.270	
ω_e	319.7	378.7	355.1	350.2	347.0	356.5	

[a] The Dunham notation is used. Bond distance R_e in Å, dissociation energy D_0^0 in eV (not corrected for spin–orbit coupling), vibrational frequency ω_e in cm^{-1}, anharmonic vibration constants $\omega_e x_e$ in cm^{-1}, and $\omega_e y_e$ in 10^{-3} cm^{-1}, rotational constant B_e in cm^{-1}, centrifugal distortion constant D_e in 10^{-8} cm^{-1}, vibration-rotation coupling constants α_e in 10^{-3} cm^{-1} and γ_e in 10^{-6} cm^{-1}, vertical IP_v and adiabatic $\mathrm{IP}_{\mathrm{ad}}$ ionization potential $^1\Sigma^+(\mathrm{InCl})\rightarrow{}^2\Sigma^+(\mathrm{InCl}^+)$ in eV, dipole moment μ_e in Debye and static dipole-polarizabilities $\alpha_\parallel$ and $\alpha_\perp$ in a.u. Masses used, ^{115}In: 114.074, ^{35}Cl: 34.7162, ^{37}Cl: 36.6989. The adiabatic IP is corrected for zero-point vibrational contributions. $\langle P\rangle$ is defined as the vibrational averaged molecular property for the ground state vibrational level $(n=0)$, i.e., $\langle 0|P|0\rangle$. Experimental results from Refs. 45, 71, and 72.

[b] Reference 73.

[c] Reference 72.

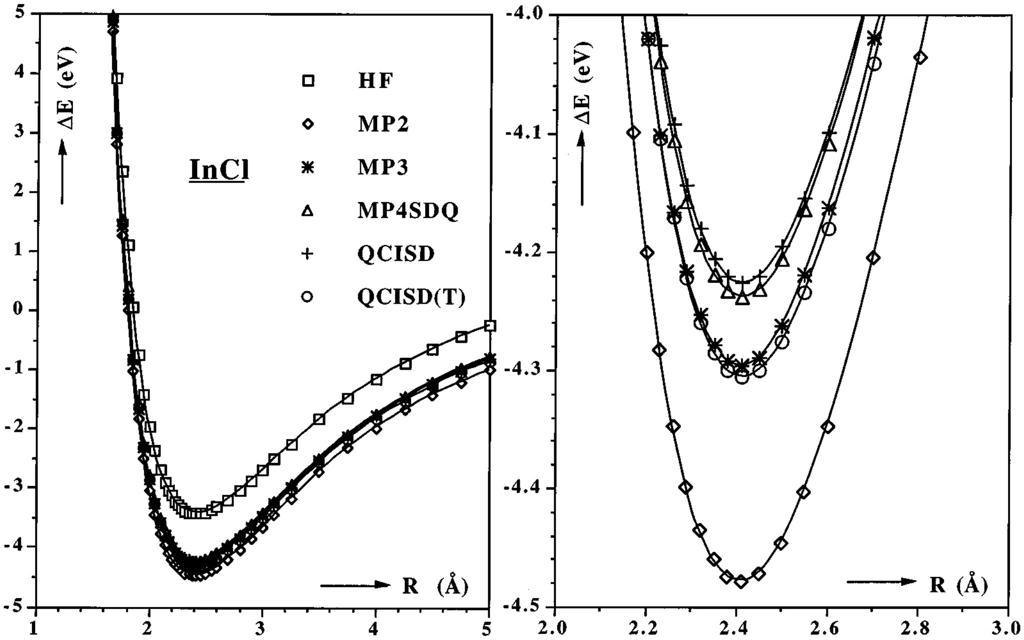

FIG. 5. $^1\Sigma^+$ ground state potential curves $\Delta E(R)$ of InCl at various levels of theory. The zero-point is chosen as the separate atom limit.

TABLE VI. Polynomial coefficients for the internuclear dependence of the molecular properties of InCl using the SEFIT PP.[a]

	ΔE	μ	$\alpha_{\parallel}$	$\alpha_{\perp}$	q
a_0	−1.5841(−1)	−1.3848(0)	7.3995(1)	4.5195(1)	−7.4281(−1)
a_1	0.	−1.5056(0)	2.0754(1)	−3.1548(0)	−6.7790(−1)
a_2	4.9026(−2)	5.5894(−3)	5.8899(0)	1.8415(0)	2.9348(−1)
a_3	−4.3694(−2)				
a_4	1.8818(−2)				
a_5	−3.7785(−3)				

[a] The formula $P(R)=a_0+a_1x+a_2x^2+\cdots$ with $x=(R-R_e)$ is used for a particular property P. ΔE, potential energy curve, μ, dipole moment, α, dipole-polarizability, q, chlorine field gradient. All values (including R) are in a.u. The coefficient a_0 defines the molecular property at the minimum bond distance R_e, i.e., for the potential energy curve ΔE we have $a_0=\Delta E(R_e)$, which is the dissociation energy D_e (not corrected for the zero-point vibrational contribution).

on InCl. A subsequent paper will compare different pseudopotential approximations using a small core definition for indium. However, for the following we decided to adopt the simple SEFIT PP without CPP and CRC corrections,[33] which leads to satisfying results for all molecular properties due to error compensation.

To summarize, the differences between the different fit procedures is 0.03 Å at most. The effect of including $V_{l>2}$ terms reduces the bond distance by about 0.04–0.05 Å. The effect of the CPP leads to a further reduction of the InCl bond distance of about 0.04 Å.

MOLECULAR PROPERTIES

The calculated spectroscopic constants for InCl are shown in Table V and compared with experimental results. As can be seen our calculated values generally agree very well with experimental results. The dissociation energies are not corrected for spin–orbit coupling. We expect, however, that the molecular spin–orbit stabilization is small compared to the atomic contribution. For the atoms we can estimate the spin–orbit stabilization using the experimental spin–orbit splitting of In and Cl resulting in a total stabilization of 21.1 kJ/mol.[37] The spin–orbit corrected dissociation energy for InCl is therefore 4.07 eV which still is in good agreement with the experimental result of 4.44 eV.[45]

Isotope effects between the ^{35}Cl and ^{37}Cl nucleus are also shown in Table V, differences in molecular properties between the two isotopes ^{113}In and ^{115}In are very small and have been omitted. The centrifugal distortion constant D_e and the vibrational-rotational coupling constant γ_e are more sensitive to isotope effects than other properties listed in Table V. This is expected as D_e and γ_e are connected to the Dunham coefficients[74] Y_{02} and Y_{21} which are roughly proportional to μ^{-2} in contrast to the harmonic frequency which behaves $\sim\mu^{-1/2}$.

The following polynomial ansatz for a certain molecular property $P(R)$ of InCl is taken:

$$P(R)=a_0+a_1x+a_2x^2+\cdots\ , \tag{7}$$

where $x=(R-R_e)$, R is the internuclear distance and R_e the minimum of the potential curve $\Delta E(R)$ shown in Fig. 5. The polynomial coefficients are listed in Table VI. With a polynomial like (7) for $\Delta E(R)$, the potential curve can easily be transformed into a Dunham series[74] or into some modified Dunham series.[44] These coefficients can be used for calculating the vibrational-rotational behavior of molecular properties.

At the QCISD(T) level we obtain the following approximate formulas for the dependence of molecular properties on the vibrational quantum state $|n\rangle$ (the number of significant digits do not reflect the accuracy of the calculation but rather shows more precisely the n-dependence),

$$\text{internuclear distance (Å):}\quad R_n=2.4182+0.0081n$$

$$\text{dipole moment } (D)\text{:}\quad \mu_n=-3.5490-0.0583n$$

$$\text{dipole polarizabilities (a.u.):}\quad \alpha_{\parallel_n}=74.198+0.411n$$

$$a_{\perp_n}=45.187-0.021n-0.001n^2.$$

For the EFG at the MP2 level we have (in a.u.),

$$q_n=14.180+0.091n\quad \text{for } ^{35}\text{Cl}$$

$$q_n=11.175+0.070n\quad \text{for } ^{37}\text{Cl}.$$

These properties show almost a linear behavior in the vibrational quantum number n (with the exception of $a_{\perp}$ having a small nonlinear term). Moreover, as shown in Figs. 6–8, the dependence of the dipole moment, polarizabilities and EFG on the internuclear distance is almost perfectly linear and therefore, the dependence on the vibrational state shown above arises mainly from the anharmonic behaviour of the potential curve (mechanical anharmonicity).[47]

Hoeft *et al.* obtained the experimental dipole moment from Stark-effect measurements on the rotational transitions $J=1\rightarrow2$.[71] They obtained μ=3.79±0.1 D for ^{115}In^{35}Cl and μ=3.84±0.1 D for ^{115}In^{37}Cl. It is not clear if the difference between the two values is a true isotope effect or due to the relatively large experimental error. Our calculations show that isotope effects are very small; for ^{115}In^{37}Cl we obtain $\mu(0)=-3.5484$ D, $\alpha_{\parallel}(0)=74.192$ a.u. and $a_{\perp}(0)=45.185$

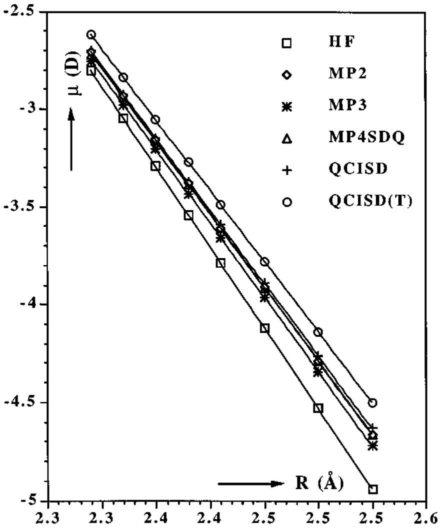

FIG. 6. Distance dependent dipole moment curve $\mu(R)$ for InCl.

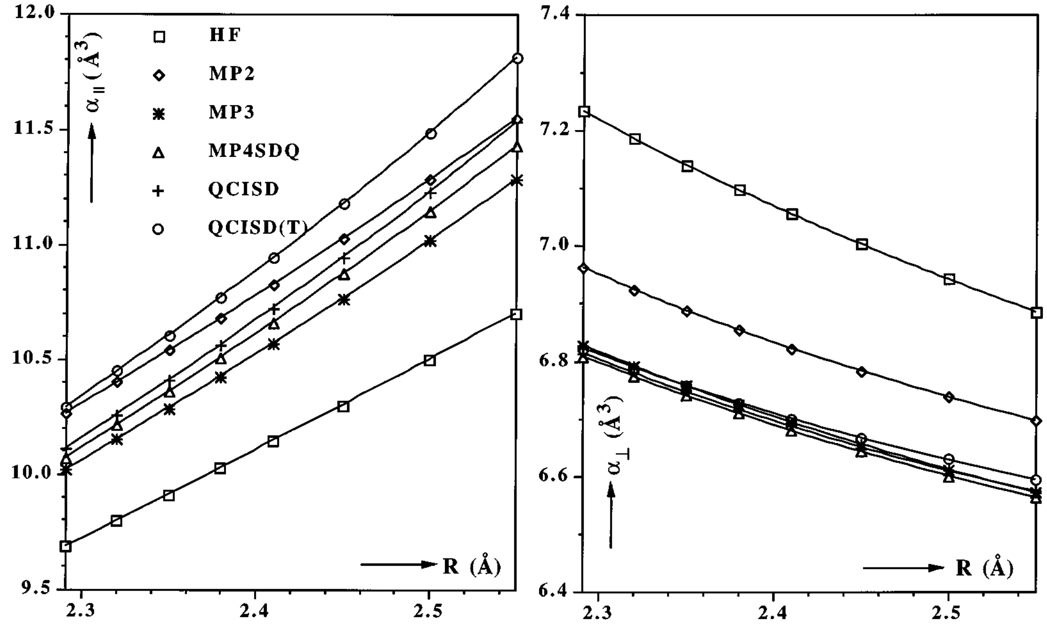

FIG. 7. Static dipole-polarizability curves $\alpha(R)$ for the parallel ($\alpha_{\parallel}$) and perpendicular ($\alpha_{\perp}$) component.

a.u. Hence, the difference between ^{115}In^{35}Cl and ^{115}In^{37}Cl is as small as 0.0006 D. Furthermore, in contrast to the experiment our calculated ^{115}In^{37}Cl dipole moment is smaller than the ^{115}In^{35}Cl dipole moment.

Hoeft[75] obtained chlorine NQCCs from hyperfine measurements (in MHz, ^{115}In^{35}Cl, -13.28 ± 0.21; ^{115}In^{37}Cl, -10.11 ± 0.45) which are in very good agreement with our MP2 results (in MHz, ^{115}In^{35}Cl, -14.18, ^{115}In^{37}Cl, -11.18). The two curves q_n for the chlorine EFG of ^{115}In^{35}Cl and ^{115}In^{37}Cl are shown in Fig. 9. Differences between the two isotopes are small and become slightly larger with increasing vibrational quantum number n. However, we point out that the calculated EFG curves do not show the correct long distance behavior, i.e., they do not approach the correct value for the EFG of the chlorine radical as R approaches infinity. Our closed shell SCF procedure forces a dissociation into the ionic fragments In$^+$ and Cl$^-$ and therefore, $q(\text{InCl})\rightarrow 0$ if $R\rightarrow\infty$. Even MP2 cannot correct this behavior, i.e., at a distance of ~3.25 Å both curves have a minimum. To avoid such anomalies, a multireference electron correlation procedure would be necessary. However,

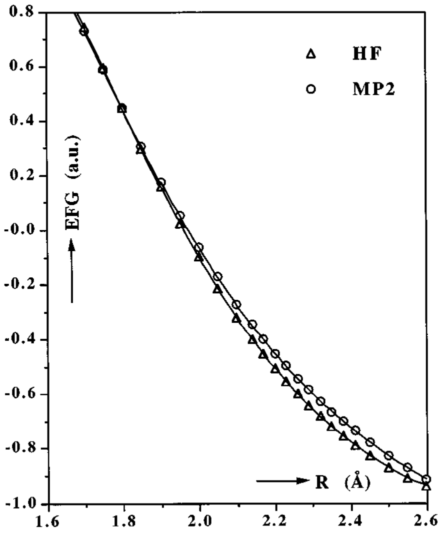

FIG. 8. Distance dependent electric field gradient curves $q(R)$ at the HF and MP2 level of theory.

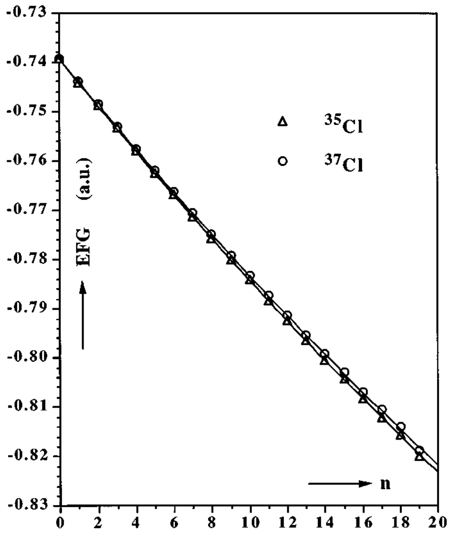

FIG. 9. MP2 electric field gradient dependence on the vibrational quantum number q_n for chlorine. The two isotopes ^{115}In^{35}Cl and ^{115}In^{37}Cl are used in the vibrational analysis.

around the equilibrium bond distance the curves should be reliable as can be seen by comparison of the calculated NQCCs with the experimental values (Table V). For example, the anisotropy in the dipole-polarizability is (Table VI),

$$\gamma=\alpha_{\parallel_n}-a_{\perp_n}\approx 28.8+23.9x+4.0x^2$$

around the minimum R_e. Since $\gamma\rightarrow 0$ for $R\rightarrow\infty$, we conclude that there is a maximum in γ at large In–Cl distances. This shows again that our approximate formulas (Table VI) can be used only around the minimum.

The indirect isotope effect in the chlorine NQCC resulting from the difference between ^{115}In and ^{113}In is very small and the calculated difference in NQCC between ^{113}In^{35}Cl and ^{113}In^{35}Cl is 1×10^{-4} MHz for the vibrational ground state ($n=0$). The reported difference between ^{113}In^{35}Cl: (-13.0 ± 1.4) and ^{115}In^{35}Cl (-13.21 ± 0.21) is therefore again due to the large experimental error.

Dobbs and Hehre carried out all-electron calculations using a 3-21G basis set ($r_e=2.504$ Å and μ=4.8 D) as well as a 3-21G* basis set ($r_e=2.470$ Å and μ=3.8 D).[25] The difference in their two dipole moments demonstrates the importance of polarization functions. Their HF results[25] at the 3-21G* level compare well with our HF PP values (Table V). Von Niessen used Green's function methods (GF) with an extended Huzinaga basis set to determine the vertical ionization potential of InCl.[26] Using an outer valence GF he obtains 9.21 eV which is in good agreement with our QCISD(T) result of 9.23 eV. A Tamm-Dancoff GF yields 8.99 eV.[26] However, the experimental value for the vertical IP is 9.75 eV.[73] We assume that in order to achieve a more accurate result core-valence correlation must be accounted for. In Table V we also list the bond distance R_e and harmonic frequency ω_e of InCl$^+$, experimental values are not available.

Balasubramanian carried out CASSCF calculations[24] followed by a second-order CI using Hay–Wadt pseudopotentials[27,28] ($r_e=2.37$ Å, $\omega_e=296$ cm^{-1}, $\mu_e=3.0$ D, $D_0=4.2$ eV). Again, we see a typical small bond distance for InCl due to the core definition of the indium pseudopotential. However, as shown above by MRCI calculations valence correlation has only little effect on the InCl bond distance and our MP2 value with the Hay–Wadt PP is 2.39 Å. We therefore conclude, that the basis sets used by Balasubramanian are not adequate. As mentioned before, these authors calculated a relatively low value for the dipole-moment which they attributed to the fact that an experimentally determined dipole moment would be the vibrational averaged property, $\mu(0)$, which should be higher than the dipole moment calculated at the equilibrium distance, μ_e. Table V shows that vibrational averaging increases the dipole moment by only 0.03 D (!). We conclude that the large errors are most likely due to the small basis set used in their study.

The results for InCl$_3$ are listed in Tables VII and VIII. The decomposition energy $\Delta E(\mathrm{InCl_3}\rightarrow\mathrm{InCl}+\mathrm{Cl_2})$ should be corrected by zero-point vibrational contributions (ZPVC). However, for this decomposition we obtain only 3 kJ/mol ZPVC using experimental vibrational data (Tables V, VIII, and Ref. 45), which can be neglected. Nevertheless, ΔE +ZPVC calculated for this reaction is 335 kJ/mol. Table VII shows that the decomposition energy for InCl$_3$ is not very dependent upon the electron correlation method used and even HF produces a quite reliable value for ΔE, as this was found earlier for all group 13 fluorides as well as for thallium halides.[19,20] Calculations on GaF$_3$ have shown that core-valence correlation effects play only a minor role for such decomposition energies.[19] Hence, we expect that our calculated value of 335 kJ/mol should be reliable. The originally estimated decomposition energy of 201 kJ/mol (Ref. 57) can therefore be discarded. Moreover, using Barins thermodynamic values[76] listed for InCl$_3$ we estimate a decomposition energy of 302.5 kJ/mol in reasonable agreement with our computed results.

Earlier, Stevenson and Schomaker[81] determined a bond distance for InCl$_3$ of 2.46 Å by electron diffraction studies which certainly is incorrect since we expect $r_e(\mathrm{InCl_3})<r_e(\mathrm{InCl})$, as this is the case for our calculated values [however, $r_e(\mathrm{BF_3})>r_e(\mathrm{BF})$, see Ref. 19].

The harmonic frequencies are listed in Table VIII and the corresponding force field in symmetry coordinates in Table VII. Our values are in excellent agreement with experimental results. Anharmonicity effects are either small or we

TABLE VII. Molecular properties for InCl$_3$ using the SEFIT PP.[a]

	HF	MP2	MP3	MP4SDQ	QCISD	QCISD(T)	Expt.
R_e	2.284	2.292	2.292	2.292	2.295	2.299	2.28±0.01
ΔE	357.6	369.1	349.6	341.1	339.3	338.0	(302.5)[b]
f_R	0.158	0.150	0.150				
$f_{RR'}$	0.007	0.005	0.005				
f_α	0.144	0.125	0.125				
$f_{\alpha\alpha'}$	0.072	0.062	0.063				
$f_{R\alpha}$	0.015	0.013	0.013				
$f_{R\alpha'}$	−0.015	−0.013	−0.013				
f_τ	0.057	0.052	0.052				

[a] InCl$_3$ adopts the trigonal planar structure in gas phase. Bond distance R_e in Å, decomposition energy ΔE for the reaction InCl$_3$→InCl+Cl$_2$ in kJ/mol, force field f in a.u. and rad. ΔE is not corrected for zero-point vibrational energies. Internal coordinates, R bond stretch, α angle bend, τ out-of-plan motion. $f_{R\alpha'}$ is the off-diagonal force constant between the M–F bond and the adjacent FMF plane. Experimental bond distance from Refs. 56–58.

[b] Estimated decomposition energy of InCl$_3$ using the thermodynamic values of Barin (Ref. 76).

TABLE VIII. Vibrational spectrum of Incl$_3$ using the SEFIT PP.[a]

		In(115)–Cl(35)		IR/Raman gas phase expt	IR Ar-matrix expt	In(115)–Cl(37) MP3
	HF	MP2	MP3			
$\nu_1(A_1')$	360(0)	349(0)	348.2	350	359	338.7
$\nu_2(A_2'')$	115(26)	110(21)	110.0	110	104	108.5
$\nu_3(E')$	404(83)	396(73)	395.8	394	401	388.4
$\nu_4(E')$	107(15)	99(13)	99.5	94–95	101	97.2

[a] Calculated harmonic and experimental frequencies (Refs. 77–80) in cm^{-1}. The MP3 results are given to one more significant figure for better comparison of the chlorine isotope effect.

have a fortuitous error compensation in our approximation applied. Isotope effects due to the mass difference of ^{35}Cl and ^{37}Cl are relatively small (Table VIII), but measurable. Pong *et al.* discussed the ^{35}Cl/^{37}Cl isotope splitting which is 2.6 cm^{-1} for the ν_3 mode if all three ^{35}Cl are substituted by ^{37}Cl.[78] This splitting does not agree so well with our calculated value of 7.4 cm^{-1}, Table VIII.

CONCLUSION

Energy-consistent relativistic pseudopotentials were applied to calculate spectroscopic constant of InCl and InCl$_3$. They generally agree well with experimental results. The approximations were discussed in great detail for a system of three valence electron pseudopotentials of indium. We found relatively large differences for the InCl and InCl$_3$ bond distances between the different pseudopotentials in use. It is not desirable that different fitting schemes for pseudopotentials lead to such differences as this is depicted in Fig. 2. Accurately adjusted PPs should *not* deviate too much from each other in their functional form (from a certain cutoff radius $r>r_c$ on). Concerning the results presented here we cannot find a conclusion which adjustment scheme for the PP parameters is the better one. We conclude, however, that in order to achieve results of higher quality for all spectroscopic constants presented here, especially the In–Cl bond distance, small core pseudopotentials have to be used treating (at least) the indium $4d$ electrons as valence electrons. Work in this direction is underway.

The dependence of molecular properties on the vibrational structure was discussed for InCl. Except for the static dipole polarizability $\alpha_\parallel$ there is no strong behavior upon the vibrational quantum number n. Electron correlation does not seem to be important for the decomposition energy of InCl$_3$ into InCl and Cl$_2$. Isotope effects are small (except, of course, for the NQCC).

ACKNOWLEDGMENTS

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[1] P. Pyykkö, Chem. Rev. **88**, 563 (1988).

[2] (a) R. B. Ross, S. Gayen, and W. C. Ermler, J. Chem. Phys. **100**, 8145 (1994); (b) L. F. Pacios and P. A. Christiansen, *ibid*. **82**, 2664 (1985); (c) M. M. Hurley, L. F. Pacios, P. A. Christiansen, and W. C. Ermler, *ibid*. **84**, 6840 (1986); (d) L. A. Lajohn, P. A. Christiansen, R. B. Ross, T. Atashroo, and W. C. Ermler, *ibid*. **87**, 2812 (1987); (e) R. B. Ross, J. M. Powers, T. Atashroo, W. C. Ermler, L. A. Lajohn, and P. A. Christiansen, *ibid*. **93**, 6654 (1990); (f) W. C. Ermler, R. B. Ross, and P. A. Christiansen, Int. J. Quantum Chem. **40**, 829 (1991); (g) M. Dolg, H. Stoll, and H. Preuss, J. Chem. Phys. **90**, 1730 (1989); (h) W. Küchle, M. Dolg, H. Stoll, and H. Preuss, Mol. Phys. **74**, 1245 (1989); (i) D. Andrae, U. Häussermann, M. Dolg, H. Stoll, and H. Preuss, Theor. Chim. Acta **77**, 1235 (1990); (k) W. Küchle, M. Dolg, H. Stoll, and H. Preuss, J. Chem. Phys. **100**, 7535 (1994).

[3] (a) J. C. Phillips, Phys. Rev. **112**, 685 (1958); (b) J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959); (c) J. C. Phillips and L. Kleinman, Phys. Rev. **118**, 1153 (1960).

[4] (a) V. Fock, M. Wesslow, and M. Petrashen, Z. Eksperim. i. Teor. Fiz. **10**, 723 (1940); (b) J. P. Weeks, A. Hazi, and S. A. Rice, Adv. Chem. Phys. **16**, 283 (1969); (c) B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962); (d) V. Heine, and M. Cohen, Phys. Rev. **122**, 1821 (1961); (e) L. Szasz, Z. Naturforsch. **14a**, 1014 (1959); (f) L. Szasz and G. McGinn, J. Chem. Phys. **42**, 2363 (1965); (g) **45**, 2898 (1966); (h) **47**, 3495 (1967); (i) G. McGinn, J. Chem. Phys. **58**, 772 (1973); (k) M. T. Yin, and M. L. Cohen, Phys. Rev. B **25**, 7403 (1982).

[5] S. Huzinaga, D. McWilliams, and A. A. Cantu, Adv. Quantum Chem. **7**, 187 (1973).

[6] (a) G. L. Malli and N. C. Pyper, Proc. R. Soc. London, Ser. A **407**, 377 (1986); (b) G. L. Malli, in *Molecules in Physics, Chemistry and Biology*, edited by J. Maruani (Kluwer, Dordrecht, 1988), Vol. 2, p. 85.

[7] (a) N. C. Pyper, Mol. Phys. **39**, 1327 (1981); (b) **41**, 949 (1981); (c) **42**, 1059 (1981); (d) **42**, 1073 (1981).

[8] (a) K. G. Dyall, P. R. Taylor, K. Faegri, and H. Partridge, J. Chem. Phys. **95**, 2583 (1991); (b) K. G. Dyall, *ibid*. **96**, 1210 (1991); (c) **98**, 2191 (1993); (d) O. Matsuoka, *ibid*. **97**, 2271 (1992).

[9] (a) V. Bonifacic and S. Huzinaga, J. Chem. Phys. **60**, 2779 (1974); (b) Y. Sakai, E. Miyoshi, M. Klobukowski, and S. Huzinaga, J. Comput. Chem. **8**, 226 (1987); (c) Y. Sakai, E. Miyoshi, M. Klobukowski, and S. Huzinaga, *ibid*. **8**, 256 (1987); (d) Z. Barandiaran, and L. Seijo, Can. J. Chem. **70**, 409 (1992); (e) S. Huzinaga, L. Seijo, Z. Barandiaran, and M. Klobukowski, J. Chem. Phys. **86**, 2132 (1987); (f) L. Seijo, Z. Barandiaran, and S. Huzinaga, *ibid*. **91**, 7011 (1989); (g) Z. Barandiaran, L. Seijo, and S. Huzinaga, *ibid*. **93**, 5843 (1990).

[10] (a) S. N. Datta, C. S. Ewig, and R. Van Wazer, Chem. Phys. Lett. **57**, 83 (1978); (b) Y. Ishikawa, and G. Malli, J. Chem. Phys. **75**, 5423 (1981); (c) Y. Ishikawa, in *Relativistic Effects in Atoms, Molecules and Solids*, NATO ASI Series B: Physics, edited by G. Malli (Plenum, London, 1983), Vol. 87, p. 363.

[11] E. Van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).

[12] W. H. E. Schwarz, Phys. Scr. **36**, 403 (1987).

[13] Compare the relativistic corrections for Au$_2$ derived from different relativistic procedures. (a) P. Schwerdtfeger, Chem. Phys. Lett. **183**, 457

(1991); (b) E. Van Lenthe, E. J. Baerends, and J. G. Snijders (personal communication, 1993); (c) B. Hess (personal communication, 1993); (d) O. D. Häberlen and N. Rösch, Chem. Phys. Lett. **199**, 491 (1992); (e) T. Bastug, D. Heinemann, W. D. Sepp, D. Kolb, and B. Fricke, *ibid.* **211**, 119 (1993).

[14] (a) T. Leininger, J. F. Riehl, G. H. Jeung, and M. Pelissier, Chem. Phys. Lett. **205**, 301 (1990); (b) D. Andrae, M. Dolg, H. Stoll, and W. C. Ermler, *ibid.* **220**, 341 (1994); (c) U. Steinbrenner, A. Bergner, M. Dolg, and H. Stoll, Mol. Phys. **82**, 3 (1994).

[15] (a) G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982). See also (b) P. J. Deuteneer, W. vanHaeringen, F. Brusens, J. T. Devreese, O. H. Nielsen, P. E. VanCamp, and V. E. VanDoven, Phys. Rev. B **37**, 4795 (1988); (c) G. B. Bachelet, D. R. Hamann, and M. Schlüter, *ibid.* **37**, 4798 (1982).

[16] M. Klobukowski, Theor. Chim. Acta **83**, 239 (1992).

[17] Y. Ishikawa, G. L. Malli, and N. C. Pyper, Chem. Phys. Lett. **194**, 481 (1992).

[18] C. Froese-Fischer, *The Hartree-Fock Method for Atoms, A Numerical Approach* (Wiley, London, 1977).

[19] P. Schwerdtfeger, G. A. Heath, M. Dolg, and M. A. Bennett, J. Am. Chem. Soc. **114**, 7518 (1992).

[20] P. Schwerdtfeger, and J. Ischtwan, J. Mol. Struct. (THEOCHEM) **306**, 9 (1994).

[21] P. Schwerdtfeger, P. D. W. Boyd, S. Brienne, and A. K. Burrell, Inorg. Chem. **31**, 3411 (1992).

[22] K. Raghavachari and G. W. Trucks, J. Chem. Phys. **91**, 1062 (1989).

[23] A. H. Barrett, and M. Mandel, Phys. Rev. **109**, 1572 (1958).

[24] K. Balasubramanian, J. X. Tao, and D. W. Liao, J. Chem. Phys. **95**, 4905 (1991).

[25] K. D. Dobbs, and W. J. Hehre, J. Comput. Chem. **7**, 359 (1986).

[26] W. Von Niessen, J. Electron. Spectrosc. Relat. Phenom. **37**, 187 (1986).

[27] P. J. Hay, and W. R. Wadt, J. Chem. Phys. **82**, 284 (1985).

[28] P. J. Hay, and W. R. Wadt, J. Chem. Phys. **82**, 299 (1985).

[29] G. A. L. Delvigne and H. W. deWijn, J. Chem. Phys. **45**, 3318 (1966).

[30] B. Schenk, E. Tiemann, and J. Hoeft, Z. Naturforsch. **25a**, 1827 (1970).

[31] (a) R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989); (b) J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987); (c) J. Paldus, J. Cizek, and B. Jeziorski, *ibid.* **90**, 4356 (1989); (d) **93**, 1485 (1990); (e) K. Raghavachari, M. Head-Gordon, and J. A. Pople, *ibid.* **93**, 1486 (1990).

[32] C. Møller, and M. S. Plesset, J. Chem. Phys. **46**, 618 (1934).

[33] G. Igel-Mann, H. Stoll, and H. Preuss, Mol. Phys. **65**, 1321 (1988).

[34] P. Schwerdtfeger, H. Stoll, and H. Preuss, J. Phys. B **15**, 1061 (1982).

[35] Ph. Durand, and J. C. Barthelat, Theor. Chim. Acta **38**, 283 (1975).

[36] (a) D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979); (b) W. E. Pickett, Comput. Phys. Rep. **9**, 115 (1989); (c) P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, J. Chem. Phys. **71**, 4445 (1979).

[37] C. E. Moore, Natl. Bur. Stand. U.S. Circ. 1958.

[38] K. S. Bhatia, J. Phys. B **11**, 2421 (1978).

[39] The $(4s/4p)$ set is from Durand *et al.* (Ref. 40) extended by a $(3s/2p/1d)$ set with exponents (0.4,0.03,0.01/0.45,0.015/0.16).

[40] J. C. Barthelat, M. Pelissier, P. Villemur, R. Devilliers, G. Trinquier, and Ph. Durand, Program PSHONDO (PSATOM), Manuel d'utilisation, Universite de Paul Sabatier, Toulouse, France, 1981.

[41] T. H. Dunning, Chem. Phys. Lett. **7**, 423 (1970).

[42] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, J. B. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart and J. A. Pople, GAUSSIAN92/DFT, Revision F.3, Gaussian Inc., Pittsburgh, PA, 1993.

[43] K. Andersson, M. R. A. Blomberg, M. P. Fülscher, V. Kellö, R. Lindh, P.-Aa. Malmqvist, J. Noga, J. Olsen, B. O. Roos, A. J. Sadlej, P. E. M. Siegbahn, M. Urban, and P.-O. Widmark, MOLCAS, Version 2, University of Lund, Sweden, 1991.

[44] S. Wilson, in *Methods in Computational Chemistry*, edited by S. Wilson (Plenum, New York, 1992), Vol. 4, p. 1.

[45] (a) K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. IV, Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979); (b) J. Hoeft and K. P. R. Nair, Chem. Phys. Lett. **155**, 273 (1989).

[46] T. Fischer, program MOLVIB, ETH Zürich, 1994.

[47] D. M. Bishop, Rev. Mod. Phys. **62**, 343 (1990).

[48] P. Pyykkö, and J. Li, Nuclear Quadrupole Moments, Report HUKI 1-92, ISSN 0784-0365, University of Helsinki, 1992.

[49] (a) W. H. E. Schwarz, Theoret. Chim. Acta **11**, 307 (1968); (b) **23**, 147 (1968); (c) T. C. Chang, P. Habitz, B. Pittel, and W. H. E. Schwarz, *ibid.* **34**, 263 (1974); (d) T. C. Chang, P. Habitz, and W. H. E. Schwarz, *ibid.* **44**, 61 (1977).

[50] B. Pittel, and W. H. E. Schwarz, Chem. Phys. Lett. **46**, 121 (1977).

[51] Ch. Teichteil, J. P. Malrieu, and J. C. Barthelat, Mol. Phys. **33**, 181 (1977).

[52] U. Wedig, M. Dolg, and H. Stoll, in *Quantum Chemistry: The Challenge of Transition Metals and Coordination Chemistry*, edited by A. Veillard (Reidel, Dordrecht, 1986).

[53] P. Durand and J. C. Barthelat, Chem. Phys. Lett. **38**, 283 (1975).

[54] A. Bergner, M. Dolg, W. Küchle, H. Stoll, and H. Preuss, Mol. Phys. **80**, 1431 (1993).

[55] L. A. Lajohn, P. A. Christiansen, R. B. Ross, T. Atashroo, and W. C. Ermler, J. Chem. Phys. **87**, 2812 (1987).

[56] N. Vogt, A. Haaland, K. G. Martinsen, and J. Vogt, J. Mol. Spectrosc. **163**, 515 (1994).

[57] A. Haaland, A. Hammel, K. G. Martinsen, J. Tremmel, and H. V. Volden, J. Chem. Soc. Dalton Trans. **1992**, 2209.

[58] G. V. Girichev, N. I. Giricheva, V. A. Titov, and T. P. Chusova, Zh. Strukt. Khim. **33**, 36 (1992).

[59] (a) C. Bottcher, and A. Dalgarno, Proc. Soc. London, Ser. A **340**, 187 (1974); (b) G. Peach, in *Long-Range Interactions in Atoms and Diatomic Molecules, Atoms in Astrophysics*, edited by P. G. Burke, W. B. Eissner, D. G. Hummer, and I. C. Percival (Plenum, London, 1983).

[60] (a) W. Müller, W. J. Flesch, and W. Meyer, J. Chem. Phys. **80**, 3297 (1984); (b) W. Müller and W. Meyer, *ibid.* **80**, 3311 (1984).

[61] P. Hafner, and W. H. E. Schwarz, J. Phys. B **11**, 2975 (1978).

[62] (a) P. Fuentealba, H. Preuss, H. Stoll, and L. v. Szentpaly, Chem. Phys. Lett. **89**, 418 (1982); (b) L. v. Szentpaly, P. Fuentealba, H. Preuss, and H. Stoll, *ibid.* **93**, 555 (1982); (c) P. Fuentealba, H. Stoll, L. v. Szentpaly, P. Schwerdtfeger, and H. Preuss, J. Phys. B **16**, L323 (1983).

[63] P. Fuentealba, L. v. Szentpaly, H. Preuss, and H. Stoll, J. Phys. B **18**, 1287 (1985).

[64] P. Schwerdtfeger, and H. Silberbach, Phys. Rev. A **37**, 2834 (1988); **42**, 665(E) (1990).

[65] H. J. Werner and P. J. Knowles, program MOLPRO, University of Stuttgart, 1994; A. Nicklass, modified version for core-polarization potentials.

[66] P. Schwerdtfeger, Ph.D. thesis, Stuttgart, 1986.

[67] (a) A. Bernier, Ph.Millie, and M. Pelissier, Chem. Phys. **106**, 195 (1986); (b) P. Schwerdtfeger, P. D. W. Boyd, S. Brienne, J. S. McFeaters, M. Dolg, M. S. Liao, and W. H. E. Schwarz, Inorg. Chim. Acta **213**, 233 (1993); (c) P. Schwerdtfeger and J. Ischtwan, J. Comput. Chem. **14**, 913 (1993); (d) H. Stoll, P. Fuentealba, M. Dolg, J. Flad, L. v. Szentpaly, and H. Preuss, J. Chem. Phys. **79**, 5532 (1983).

[68] Program MCDF81, I. P. Grant, B. J. McKenzie, P. H. Norrington, D. F. Mayers, and N. C. Pyper, Comput. Phys. Commun. **21**, 207 (1980).

[69] (a) Program MCHF77, C. Froese-Fischer, Comput. Phys. Commun. **14**, 145 (1978); modified version by M. Dolg; (b) J. H. Wood and A. M. Boring, Phys. Rev. B **18**, 2701 (1978).

[70] G. Igel-Mann, M. Dolg, U. Wedig, H. Stoll, and H. Preuss, J. Chem. Phys. **86**, 6348 (1987).

[71] E. Tiemann, J. Hoeft, and T. Törring, Z. Naturforsch. **27a**, 869 (1972).

[72] R. D. Johnson, D. V. Dearden, and J. W. Hudgens, J. Chem. Phys. **100**, 3422 (1994).

[73] J. Berkowitz and J. L. Dehmer, J. Chem. Phys. **57**, 3194 (1972).

[74] J. L. Dunham, Phys. Rev. **41**, 721 (1932).

[75] J. Hoeft, Z. Phys. **163**, 262 (1961).

[76] I. Barin, *Thermochemical Data of Pure Substances* (VCH, Weinheim, 1993).

[77] G. K. Selivanov, and A. A. Maltsev, Zh. Strukt. Khim. **14**, 943 (1973).

[78] P. G. Pong, A. E. Shirk, and J. S. Shirk, J. Mol. Spectrosc. **66**, 35 (1977).

[79] I. R. Beattie and J. R. Horder, J. Chem. Soc. **1969**, 2655.

[80] I. R. Beattie, H. E. Blayden, S. M. Hall, S. N. Jenny, and J. S. Ogden, J. Chem. Soc. Dalton Trans. **1976**, 666.

[81] D. P. Stevenson and V. Schomaker, J. Am. Chem. Soc. **64**, 2514 (1942).