Determination of spectroscopic constants and anharmonic force-fields for HOCl and DOCl using Scaled External Correlation

Hongzhi Zhang and B. Ramachandran*

Chemistry, College of Engineering and Science, Louisiana Tech University, Ruston, Louisiana 71272, USA

Jörg Senekowitsch

Friedrichstr. 23, 61440 Oberursel, Germany

Robert E. Wyatt

Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712, USA

Abstract

We report spectroscopic constants and anharmonic force fields for the HOCl and DOCl molecules in the gas phase, calculated from *ab initio* and scaled *ab initio* potential surfaces. The *ab initio* calculations were performed at the CASSCF/MR-CISD levels of theory, using the highly polarized correlation consistent augmented Valence Triple Zeta (cc-pAVTZ) basis sets of Dunning. The multireference analog of the Davidson correction was used to approximate the effect of higher excitations (MR-CISD+Q). The Scaled External Correlation (SEC) method of Brown and Truhlar was used to extract additional dynamical correlation energy from both the MR-CISD (CI/SEC) and MR-CISD+Q (CI+Q/SEC) energies. The CI, CI+Q, CI/SEC, and the CI+Q/SEC energies up to 20 000 cm^{-1} above the HOCl minimum were fitted to polynomial expansions and the spectroscopic parameters evaluated in each case. These results are compared to those from the calculations of Koput and Peterson using significantly larger basis sets [Chem. Phys. Lett. 283 (1998) 139], the "complete basis set limit" results of Skokov *et al.* [J. Chem. Phys. 109 (1998) 2662], and to available experimental results. It is seen that applying the SEC scaling to CI or CI+Q energies obtained using a moderate basis set (cc-pAVTZ) is a viable alternative to the use of extremely large basis sets.

Keywords: Scaled External Correlation, HOCl, DOCl, spectroscopic constants, force fields.

*Corresponding author (ramu@chem.latech.edu)

1 Introduction

Extremely accurate calculations of spectroscopic constants and anharmonic force fields for small molecular systems have become possible in recent years. The *ab initio* potential energy surfaces for H_2O obtained by Partridge and Schwenke [1] and by Kedziora and Shavitt [2], and for HOCl by Peterson [3], Koput and Peterson (KP, hereafter) [4], and the more recent work by Skokov, Peterson and Bowman (SPB, hereafter) [5], are examples. These calculations have established new standards of agreement between theory and experiment, and may be said to represent the current state of the art in the field. To a considerable extent, these advances were made possible by the development of the family of progressively larger correlation-consistent polarized "Valence-n-Zeta" (cc-pVnZ) basis sets by Dunning and coworkers [6–8], where n denotes the number of exponential parameters used. To date, double (VDZ), triple (VTZ), quadruple (VQZ) [6–8], quintuple (V5Z) [4], and hextuple (V6Z) [9] zeta basis sets have been described and used in calculations. These basis sets and their "augmented" analogs, denoted as cc-AVnZ, obtained by adding diffuse functions to the standard VnZ basis sets, are designed so that the use of successively larger members of a family in a method for solving the Schrödinger equation for the electronic wavefunction yields systematic convergence to the asymptotic "complete basis set (CBS) limit" which, in principle, represents the result of using an infinitely large basis set.

The recent *ab initio* studies of the HOCl molecule [3,4] have employed the coupled cluster method [CCSD(T)] [10] in successively larger calculations up to the V5Z basis set. The study by SPB [5] utilized multireference configuration interaction with single and double excitations (MR-CISD, or simply CI) [11] employing the AVDZ, AVTZ, and AVQZ basis sets, followed by the application of the multireference analog [12] of the Davidson correction [13] to estimate the effect of higher (quadruple) excitations. The Davidson corrected energies (MR-CISD+Q, or simply CI+Q) were then extrapolated to the CBS limit, fitted to analytic expressions, and used to compute spectroscopic properties. Although these calculations yield exceptionally good agreement with experimental values for the spectroscopic properties and vibrational energy levels of the molecule, they are also exceptionally resource-intensive and time-consuming even on modern high performance computers. In fact, without the internal contraction method of Werner and Knowles [14], which substantially decreases the number of configurations in the CI expansions, these calculations may very well be intractable even for triatomic molecules. The calculations on H_2O by Kedziora and Shavitt [2], for example, employing a slightly smaller version of the Dunning cc-pAVQZ basis (the diffuse g and f functions removed from O and H, respectively), involved an uncontracted CI expansion of 3.6 million configurations. On the other hand, the AVQZ basis set for HOCl used by SPB [5], with the internal contraction algorithm, gave rise to "just over 650 000 variational parameters, which is comparable to a conventional uncontracted calculation that would have resulted in over 36 million."

The purpose of the present study is to examine whether it is possible to approach the accuracy of these "state-of-the-art" calculations using substantially smaller basis sets, but employing a semi-empirical procedure to extract the missing dynamical correlation energy. The procedure we

use to recover correlation energy is the "Scaled External Correlation" (SEC) method of Brown and Truhlar [15]. In contrast to the Davidson correction, which is based on the expansion coefficients of the CI wavefunction, the SEC procedure uses empirical information, typically experimental dissociation energies of the diatomic fragments, to estimate the fraction of the "external" or dynamical correlation energy unrecovered by the CI calculation. The SEC method has been used to develop potential energy surfaces for the F + H_2 [16, 17], Cl + H_2 [18] and, more recently, the O(^3P) + HCl reactions [19, 20].

The molecules chosen for this study, namely HOCl and its deuterated analog DOCl, are good candidates for this investigation for the following reasons. It is obvious from the above description that achieving near-spectroscopic accuracy for this system is extremely difficult and computationally challenging. Our own *ab initio* calculations [21], as well as those of Peterson [3] and KP [4], have shown that it is especially hard to recover dynamical correlation energy from the ClO fragment using moderate basis sets. This makes the use of the SEC procedure in the present system almost unavoidable if one wishes to recover as much correlation energy as possible without resorting to extremely large basis sets. Another reason is that, in addition to the availability of the calculations cited above, several accurate experimental determinations of the equilibrium geometry and spectroscopic constants of HOCl are available [22–28], as are anharmonic force fields determined by combining experimental data with calculations at the SCF [29] and MP3 [30] levels of theory. A fair amount of information is available for DOCl as well [26, 31]. This makes it possible to compare the results of our calculations not only to other *ab initio* results, but to accurate experimental observations.

The remainder of this paper is organized as follows. In the following Section, we provide some details of the *ab initio* calculations, the scaling procedure, fitting of the energies, and the calculation of the spectroscopic properties. In Section III, the results of the present study are compared to those of KP, SPB, and to available experimental data. Section IV is a discussion which highlights the major conclusions from this work.

2   Methods

2.1   Ab Initio Calculations

The *ab initio* energies for the diatomic fragments, HCl, OH and ClO, as well as the triatomic species HOCl were calculated initially at the CASSCF level of theory, and the CAS wavefunctions were then used as references for the internally contracted MRCI method of Werner and Knowles [14], as implemented in MOLPRO92 [32]. As mentioned above, the Dunning cc-pAVTZ basis set was used. The core orbitals were treated as closed shells in the CAS step. For the HOCl molecule, the CI calculations correlated all fourteen valence electrons, but did not include the effects of core-valence correlation. The calculations for the diatomic fragments, performed as two-body problems rather than as three-body problems with the third atom at a large distance, were done using similar steps. Since these were primarily aimed at obtaining accurate estimates of the diatomic dissociation energies to be used in SEC scaling (see below), the lack of size-extensivity of the MR-CISD method was not an issue.

It is important to note that these calculations are far less demanding than the V5Z [4] and AVQZ [5] calculations described earlier. The full valence active space for our calculations, which includes all molecular orbitals arising out of the nine valence atomic orbitals, consisted of 302 configuration state functions (CSF's) in C_s symmetry. The MRCI wavefunction, constructed from CASSCF orbitals, included slightly less than 325 000 configurations contracted from an uncontracted total of just over 16 million. This is roughly half the size of the 650 000/36 million configuration AVQZ calculation of SPB [5], and also smaller than the V5Z calculation of KP [4]. The total computing time (CASSCF followed by MRCI) was about 1500 seconds per geometry on a single CPU of a Cray J90 using less than 8 megawords (64Mb) of memory.

The diatomic energies were calculated for $0.60r_e \leq r \leq 30a_0$, with a smaller interval between points for $0.60r_e \leq r \leq 2.0r_e$. The asymptotic CAS and CI energies were converged in all cases to better than 10^{-6} hartree with respect to interatomic distance, and thus allowed for reliable estimates of the bond dissociation energies. The calculations on HOCl covered a nonuniform grid of points in the range $1.5a_0 \leq r_{OH} \leq 3.0a_0$, $2.5a_0 \leq r_{ClO} \leq 4.5a_0$, at $\theta_{HOCl} = 80, 90, 102.96, 110,$ and 120 degrees. A total of 134 points were mapped out in this region, with a higher density of points near the (expected) equilibrium geometry of the molecule, but only a subset of these points were used to generate the potential energy surfaces described below.

2.2   Scaled External Correlation

It is useful to think of correlation energy as consisting of two parts: "internal" or "non-dynamical" correlation, which arises from rearrangements of electrons in open shell and nearly degenerate orbitals, and "external" or "dynamical" correlation, arising from the instantaneous correlated motion of electrons [33]. The internal correlation depends not only on the number of electrons but also on the geometry and is, therefore, unscalable. Typically, a multiconfiguration self-consistent field (MCSCF) calculation or, since excitations from core orbitals can be neglected without significant loss of accuracy, a full valence CASSCF calculation using a reasonably large basis set will recover most of the geometry-dependent (and, therefore, unscalable) internal correlation. The external correlation can, in principle, be accounted for by including, in the CI expansion, various excitations from the CAS reference configurations to virtual orbitals. However, because of rather slow convergence of the CI expansion with respect to inclusion of higher excitations, the standard practice is to truncate the expansion at single and double excitations, yielding the CISD method. This leaves a fairly large part of the external or dynamical correlation energy unaccounted for, and this deficiency typically manifests itself in the form of smaller than observed bond dissociation energies and larger than observed reaction barriers.

The scaled external correlation (SEC) method [15] is a semiempirical technique that attempts to account for all of the dynamical correlation energy remaining unrecovered after a CAS/CI calculation. The assumptions made are that (a) the core correlation energy is independent of the molecular geometry, (b) a "reasonably large one-electron basis set" will account for almost all of the geometry-dependent nondynamical correlation energy in the multiconfiguration SCF calculation, (c) the difference between the MCSCF or full valence CASSCF energy and the MR-CISD energy provides a measure of the missing dynamical correlation energy, and (d) the dynamical correlation energy is independent of geometry and can be expressed as a constant

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(i.e., geometry independent) fraction of the difference between the CAS and CI energies. In applying the SEC method, one first calculates a scaling factor for each diatomic fragment in the problem, as

$$F_{AB} = \frac{D_{e,AB}^{\text{CI}} - D_{e,AB}^{\text{CAS}}}{D_{e,AB}^{\text{Expt.}} - D_{e,AB}^{\text{CAS}}}, \tag{1}$$

where the D_e's are the dissociation energies, and obtains an average scaling factor F which, in the case of a three-atom system, is calculated as [34]

$$F = \tfrac{1}{3}\left(F_{AB} + F_{BC} + F_{AC}\right). \tag{2}$$

The SEC scaled CI energies for the three-atom system, denoted here as CI/SEC, are then obtained as

$$E_{\text{CI/SEC}} = E_{\text{CAS}} + \frac{(E_{\text{CI}} - E_{\text{CAS}})}{F}. \tag{3}$$

In the present work, we also scale the CI+Q energies (CI+Q/SEC) in this fashion, using scaling factors calculated from CI+Q diatomic dissociation energies.

Accurate application of the SEC method in this manner depends on accurate estimates of the dissociation energies of the diatomic species. This was accomplished by fitting the CAS, CI, and CI+Q energies lying within 10 000 cm^{-1} of the minimum energies for each diatomic to a sixth power polynomial expansion in Simmons-Parr-Finlan (SPF) [35] coordinates, $(1 - r^\circ/r)$, to determine the minimum energy. In these fits, the parameter r° was set equal to the location of the lowest energy in the *ab initio* data, and no attempt was made to optimize its value. The maximum rms error in the fits was 0.299 cm^{-1}. The dissociation energies were then calculated by subtracting the minimum energy obtained from the fits from the two-body *ab initio* energy at $r = 30a_0$. In each case, the asymptotic energy was converged to within 0.22 cm^{-1} with respect to changes in interatomic distance. Table I summarizes the results of these calculations and the scaling factors calculated for the CI and CI+Q energies for each diatomic. The average scaling factor F is found to be 0.76465752 for the CI energies and 0.84391954 for the CI+Q energies.

2.3 Potential Energy Surfaces

The three-body energies lying within 20 000 cm^{-1} of the lowest energy in the CAS dataset (the same geometries were chosen in the CI, CI+Q and the SEC scaled datasets) were fitted to a polynomial expansion in SPF coordinates for the O-H and Cl-O distances and powers of the cosine of the angle H-O-Cl, as follows:

$$V(r_{\text{OH}}, r_{\text{ClO}}, \theta_{\text{HOCl}}) = \sum_{i,j,k=0}^{6,6,4} C_{ijk}\left(1 - \frac{r_{\text{OH}}^\circ}{r_{\text{OH}}}\right)^i \left(1 - \frac{r_{\text{ClO}}^\circ}{r_{\text{ClO}}}\right)^j \cos^k \theta_{\text{HOCl}}; \ i + j + k \le 6. \tag{4}$$

In these fits, the values of the r° parameters were set equal to the respective interatomic distances for the minimum energy in the fitted data. The linear coefficients C_{ijk} were optimized to yield rms errors of less than 6 cm^{-1} in the case of the CI energies and less than 2 cm^{-1} in the case of CI+Q, CI/SEC and CI+Q/SEC energies. The rms errors for CI+Q and SEC scaled energies are roughly an order of magnitude larger than the rms error reported by KP, but the range of energies fitted in the present study (20 000 cm^{-1}) is about twice that of KP. It is well-known that SPF

coordinates do not behave in a physically reasonable manner once they leave the range of the coordinates covered by the data (for example, see Ref. [2]) but, for the present purposes, since the data spans far more than the region required for the computation of the spectroscopic properties, these fits are completely appropriate. We have verified that the fitted surfaces are smooth and well-behaved over the range of interest by examining contour plots at several fixed bond angles, and cuts through the surfaces as functions of the angle for fixed internuclear distances.

2.4 Spectroscopic parameters and force fields

The fitting of the three-body term and the subsequent spectroscopic analysis were carried out using the program SURFIT, written by one of us [37] and tested against Gaw *et al.*'s SPECTRO [38]. This program first transforms the expansion coefficients in Eq. (4) into dimensionless normal mode coefficients using the L-tensor algebra of Hoy, Mills and Strey [39]. The resulting normal mode force constants are then used to compute the spectroscopic constants using standard perturbation theory expansions [40] for the vibrational-rotational energy levels of the molecule. The force field for the molecule in terms of internal displacement coordinates is also obtained from SURFIT, by expressing the normal mode force field in terms of (mass-independent) internal coordinates in the usual Taylor series expansion about the equilibrium geometry, as

$$
\begin{aligned}
V(q_1, q_2, q_3) \;=\; & V_0 + \frac{1}{2!} \sum_{i,j} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \frac{1}{3!} \sum_{i,j,k} \left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} \right)_0 q_i q_j q_k \\
& + \frac{1}{4!} \sum_{i,j,k,l} \left(\frac{\partial^4 V}{\partial q_i \partial q_j \partial q_k \partial q_l} \right)_0 q_i q_j q_k q_l.
\end{aligned}
\tag{5}
$$

where the subscripts "0" signifies that the function is evaluated at the values of the coordinates corresponding to the equilibrium geometry (zero displacement). We assign $q_1 = r_{\text{OH}} - r_{\text{OH}}^e$, $q_2 = r_{\text{ClO}} - r_{\text{ClO}}^e$, and $q_3 = \theta_{\text{HOCl}} - \theta_{\text{HOCl}}^e$. Note that the second term in the expansion, which contains the first derivative of the potential with respect to the three coordinates, is omitted since it vanishes at the minimum of the potential surface. In representing the internal force field for the molecule, as in Table V, we have chosen to denote by the indices (n_1, n_2, n_3), the order of the derivative with respect to (q_1, q_2, q_3). In the second term, for example, the summation will include the terms $(2, 0, 0), (0, 2, 0), (0, 0, 2), (1, 1, 0), (1, 0, 1)$, and $(0, 1, 1)$. In more traditional notation, these would correspond to the force constants $f_{q_1 q_1}, f_{q_2 q_2}, f_{q_3 q_3}, f_{q_1 q_2}, f_{q_1 q_3}$, and $f_{q_2 q_3}$. The indices in the remaining terms are cycled in a similar manner so that all the cubic and quartic terms are included.

3 Results

The results from the present work and their comparison to those of KP, SPB and experimental data, are organized in four Tables below. The equilibrium geometry of HOCl from fits to *ab initio* and scaled energies are compared to the results of KP, the complete basis set limit results of SPB, and experimental values in Table II. The CAS level of theory is inadequate to give accurate results, and is not included in any of the comparisons. The agreement with experimental bond lengths and the bond angle improves considerably at higher levels of theory (CI and CI+Q), and

improves further with the SEC scaling of CI and CI+Q energies. It was mentioned earlier that it is especially hard to recover correlation energy from the Cl-O diatomic fragment using moderate basis sets. Such basis sets also tend to overestimate the Cl-O equilibrium bond distance and, as seen here, underestimate the H-O-Cl bond angle. Peterson [3] found that the addition of a large exponent d function to the standard cc-pAVQZ basis (denoted as cc-pAVQZ+d) greatly improved the agreement between the calculated geometry and experiment. A similar "tight" d function is also naturally present in the cc-pV5Z basis used in the work of KP [4], and a function of this type was added to the cc-pAVnZ basis sets used by SPB. Hence, the excellent agreement between the experimental Cl-O distance and results of KP and SPB can be attributed to the improvement in the basis set. However, it is seen from Table II that the SEC procedure is also able to improve the agreement between AVTZ results at the CI and CI+Q level and experiment. In fact, the CI/SEC and CI+Q/SEC geometries reported in Table II are in better agreement with experiment than those from the standard cc-pVQZ basis and comparable to those from a pared-down version of the cc-pAVQZ basis reported by Peterson [3].

Objective statements about the quality of agreement between various properties and the corresponding experimental values can be made only if some measure of the relative error is introduced. For this purpose, we define the fractional error ε for a given property P at a particular level of theory as

$$\varepsilon_P = \frac{P_{\text{Calc}} - P_{\text{Expt.}}}{P_{\text{Expt.}}}. \tag{6}$$

It is, of course, more convenient to consider the average of the ε_P values for a group of parameters that define a particular class of property. For example, in order to compare the quality of the predicted equilibrium geometry at a particular level of theory, it is useful to examine the average of the fractional errors in the two bond lengths and bond angle. In order to prevent the possible mutual cancellation of the ε_P values (since their values could be positive or negative), we average the absolute values of the ε_P values in that class and denote it as $\langle \varepsilon_P \rangle$. This quantity for the three geometric parameters of the molecule, denoted as $\langle \varepsilon_G \rangle$, is also given in Table II for each level of theory considered. It is seen that, on average, there is a three-fold decrease in the fractional error as one goes from CI to CI/SEC, and a two-fold decrease in going from CI+Q to CI+Q/SEC. When the computational effort involved in obtaining the cc-pV5Z geometries or in performing the series of computations required for extrapolation to the CBS limit are taken into consideration, the accuracy of the relatively modest CI/cc-pAVTZ/SEC calculation is very attractive.

The equilibrium geometry calculated from a fit to *ab initio* data is, of course, determined by the first derivative of the potential surface. On the other hand, the normal mode (harmonic) frequencies of the molecule are properties of the second derivatives. In order to compare the performance of the SEC scaling in this regard, Table III presents the normal mode (harmonic) frequencies $\omega_{e,i}$ and the fundamental frequencies $\omega_{0,i}$, for the HOCl and DOCl molecules. In the case of HOCl, all reported experimental values for the normal mode (harmonic) frequencies $\omega_{e,i}$ have been *calculated* from experimental fundamental frequencies $\omega_{0,i}$ using a combination of experimentally determined and *ab initio* values for anharmonic constants. We have taken the experimental values of the $\omega_{e,i}$ from Peterson's work [3], in which the values of x_{33} and x_{23} were fixed at their *ab initio* values. So there is a certain amount of uncertainty, in addition to

the experimental error, at least in $\omega_{e,2}$ and $\omega_{e,3}$ for HOCl shown in the last column of Table III. The $\omega_{0,i}$ values, on the other hand, are obtained directly from experimental data as the vibrational band origins [22–28]. In the case of DOCl, rather than calculate the "experimental" harmonic frequencies using force constants taken from various sources, we have chosen to make the comparisons with the experimental fundamental frequencies. These comparisons once again show that the CI/SEC and CI+Q/SEC results are in better agreement with the experimental values than the unscaled values. In the case of HOCl, the $\langle \varepsilon_{\omega_e} \rangle$ values indicate that the CI/SEC results are in better agreement with experiment than those of KP, which are of comparable quality to the CI+Q/SEC results. The $\langle \varepsilon_{\omega_0} \rangle$ values for the CI/SEC and KP are identical, and only slightly larger than that for SPB. In the case of DOCl, once again the $\langle \varepsilon_{\omega_0} \rangle$ values for CI/SEC and KP are almost the same.

Table III also presents rotational constants for the ground vibrational state, A_0, B_0, and C_0, for HOCl and DOCl. The average fractional errors for the present SEC results are as much as an order of magnitude larger than the cc-pV5Z results of KP for both molecules. This is not surprising since the rotational constants are determined primarily by the equilibrium geometry which the calculations of KP reproduce very accurately, due to the presence of the large exponent d functions and the higher angular momentum functions (g and h) on O and Cl in the in the cc-pV5Z basis set.

Table IV presents a comparison of the vibration-rotation coupling constants α_i^R, the centrifugal distortion coefficients D_J, etc., and the anharmonicity constants x_{ij}. The evaluation of the α's and x_{ij}'s involve higher order derivatives of the potential, while the D's depend on the ratio of the rotational constants to the frequencies. Because of this, these properties tend to depend very sensitively on the nature of the fits as well as the "shape" of the data in the near-equilibrium configurations of the system. Once again, it is clear from Table IV that the SEC procedure applied to the CI and CI+Q energies leads to a lowering of the average error $\langle \varepsilon_P \rangle$ for the properties under consideration. The improvement in the quality of the anharmonicity and vib-rotational coupling constants in going from CI to CI/SEC is, in fact, quite dramatic in that the CI/SEC results show almost a four-fold decrease in $\langle \varepsilon_x \rangle$ and more than a two-fold decrease in $\langle \varepsilon_\alpha \rangle$ over the CI results. The errors in the CI+Q/SEC results for these properties are also smaller than those in CI+Q, but the change is not as large. The accuracy of the centrifugal distortion constants do not appear to change much due to SEC scaling of the CI or the CI+Q energies although, in each case, the SEC results are better than those from the unscaled energies. However, the quality of the agreement with experimental values at all levels is relatively poor for this set of properties when compared to that of KP.

A complete force field for HOCl has not yet been determined from experimental data alone. Halonen and Ha [30] have reported an anharmonic force field for HOCl (and DOCl, since derivatives of the potential with respect to mass-independent internal coordinates determine the force field) which includes all harmonic and cubic, as well as the diagonal quartic force constants. These authors determined as many force constants as possible from available experimental data. The remaining force constants were determined by *ab initio* calculations at the MP3/DZP level of theory. The calculations of KP have provided an *ab initio* force field consisting of all force constants to the fourth order and several to fifth and sixth orders. The present set of calculations

using SURFIT yielded force fields including all force constants up to the fourth order. The force constants for which values have been reported by Halonen and Ha [30] are presented in Table V along with the results of KP [4]. In computing the average fractional errors $\langle \varepsilon_f \rangle$ for the force constants, we have only considered those constants which were determined from experimental data. The reason is that several of the MP3/DZP force constants are in very poor agreement with the present results as well as those of KP and the earlier results of Peterson [3]. In each of these cases, the present results are in reasonable agreement with the CCSD(T)/cc-pAVQZ+d results of Peterson [3] and the CCSD(T)/cc-pV5Z results of KP. Based on these comparisons, we believe that some of the MP3/DZP constants may have relatively large errors. From the $\langle \varepsilon_f \rangle$ values given in Table V, it appears that the CI/SEC force field from cc-pAVTZ calculation is of comparable quality to that of KP while the CI+Q/SEC force field yields a slightly lower average error.

4   Discussion

The purpose of the investigations reported here was to examine whether multireference configuration interaction calculations employing relatively modest basis sets coupled with a semiempirical method to extract the unrecovered dynamical correlation energy could yield equilibrium geometries, spectroscopic parameters and force fields of accuracy comparable to challenging and resource-intensive calculations employing extremely large basis sets. In order to make objective statements regarding the quality of the agreement between the present results, those of KP, SPB, and experimental values, we defined and used an average fractional error $\langle \varepsilon_P \rangle$ for each class of property. The average of the $\langle \varepsilon_P \rangle$ values reported in Tables II-V for each type of property reveals that the application of the SEC procedure to CI and CI+Q energies bring the properties into better agreement with large basis set calculations and experiment. Based on the results summarized in Tables II-V, we conclude that such an approach can, indeed, yield results of comparable accuracy. Averaging all of the $\langle \varepsilon_P \rangle$ considered, *viz.*, those for the equilibrium geometry, normal mode frequencies, ground vibrational state rotational constants, vibration-rotation coupling constants, centrifugal distortion constants, anharmonicities, and force constants, yields 0.2860 for CI, 0.1786 for CI+Q, 0.1560 for CI/SEC, and 0.1395 for CI+Q/SEC, compared to 0.1249 for the CCSD(T)/cc-pV5Z calculations of KP. These final averages indicate that the quality of potential energy surfaces constructed from SEC-scaled CI and CI+Q energies are comparable to those obtained from *ab initio* calculations using very large basis sets.

There is a possibility that the present approach is actually better than is indicated by the average fractional errors quoted above. This has to do with the differences in the distribution of *ab initio* points, the range of energies fitted, the models used for the fits, and the quality of the fits, between the present work and that of KP. The present investigation used *ab initio* points computed as part of a project to obtain an accurate global potential energy surface for the O(^1D) + HCl reaction. A subset of these points lying in the vicinity of the HOCl equilibrium (see Section II) and within 20 000 cm^{-1} of the HOCl minimum were selected for the present comparisons. This amounted to a total of 80 points. These points were fitted to a sixth order polynomial expansion in SPF coordinates for the bond distances and cosines of the angle. KP, on the other hand, fitted a set of 114 points lying within 9000 cm^{-1} of the HOCl minimum

to a polynomial expansion in terms of displacement coordinates. As best as we can determine, the spectroscopic constants were calculated in both cases using similar procedures, namely, the perturbation theory expansion employed in SURFIT [37] and SPECTRO [38]. Due to the smaller number and larger spread in the energy of the points fitted in the present study, and the resulting larger rms errors in the fits, it is possible that the present comparisons are unfavorable to the CI/SEC approach. If the same set of points calculated at the same level of theory using cc-pAVTZ and cc-pV5Z basis sets were fitted to identical models, the comparisons could be placed on a much more rigorous footing and, if the present results are any indication, could lead to even better agreement between the smaller and larger basis set calculations.

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6 References

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Table I. Diatomic dissociation energies and SEC scaling factors.				
	E_{min}(au)	E_{asymp}(au)	D_e(au)	F
HCl				
CAS	-460.12506807	-459.98001972	0.14504835	-
CI	-460.32725346	-460.16213553	0.16511793	0.81473140
CI+Q	-460.34207732	-460.17502479	0.16705253	0.89326714
Expt.[a]	-	-	0.16968172	-
OH				
CAS	-75.43952295	-75.30429983	0.13522312	-
CI	-75.63546371	-75.47149352	0.16397019	0.83096794
CI+Q	-75.64460329	-75.47846276	0.16614053	0.89370418
Expt.[a]	-	-	0.16981780	-
ClO				
CAS	-534.34164729	-534.28467426	0.05697303	-
CI	-534.70438244	-534.61756129	0.08682115	0.64827323
CI+Q	-534.74168674	-534.65042184	0.09126490	0.74478732
Expt.[a]	$-$	-	0.10301553	-
[a]Ref. [36], $D_e = D_0 - \frac{1}{2}\omega_e + \frac{1}{4}\omega_e x_e$				

Table II. Comparison of structural parameters of HOCl.							
	CI	CI+Q	CI/SEC	CI+Q/SEC	KP	SPB	Expt.
$r_{OH}(a_0)$	1.82437	1.82720	1.82145	1.82557	1.8219	1.8189	1.82240
$r_{ClO}(a_0)$	3.24074	3.23673	3.21210	3.21878	3.1970	3.1969	3.19169
θ_{HOCl}(deg.)	101.786	102.193	102.623	102.775	102.85	102.8	102.965
$\langle \varepsilon_G \rangle$	0.00930	0.00808	0.00341	0.00403	0.00102	0.00172	-

	CI	CI+Q	CI/SEC	CI+Q/SEC	KP	SPB	Expt.
Table III. Comparison of vibrational frequencies and rotational constants for HOCl. All quantities are in cm^{-1}.							
	HOCl						
$\omega_{e,1}$	3795.3	3783.8	3822.0	3807.2	3801.8	3811.0	3797.1[a]
$\omega_{e,2}$	1266.9	1264.5	1273.0	1266.1	1276.2	1283.7	1272.1[b]
$\omega_{e,3}$	713.7	720.8	739.2	736.7	744.1	738.4	739.3[b]
$\langle \varepsilon_{\omega_e} \rangle$	0.01308	0.01152	0.00245	0.00363	0.00365	0.00467	-
$\omega_{0,1}$	3628.5	3611.5	3642.8	3626.2	3618.8	3623.1	3609.5[c]
$\omega_{0,2}$	1241.8	1233.6	1242.0	1231.5	1243.5	1245.9	1238.6[c]
$\omega_{0,3}$	705.4	708.2	725.6	720.2	729.6	723.78	724.4[c]
$\langle \varepsilon_{\omega_0} \rangle$	0.0113	0.0090	0.0046	0.0054	0.0046	0.0035	-
A_0	20.2324	20.2428	20.4518	20.3882	20.4818	-	20.46362[c]
B_0	0.4931	0.4940	0.5013	0.4991	0.50455	-	0.50429[c]
C_0	0.4813	0.4822	0.4893	0.4871	0.49160	-	0.49124[c]
$\langle \varepsilon_R \rangle$	0.01791	0.01653	0.00348	0.00747	0.00071	-	-
	DOCl						
$\omega_{0,1}$	2677.7	2665.3	2689.3	2676.8	2671.8	-	2665.6[d]
$\omega_{0,2}$	909.6	905.0	911.1	904.4	911.8	-	909.6[d]
$\omega_{0,3}$	701.9	706.0	723.8	719.2	728.2	-	723.3[d]
$\langle \varepsilon_{\omega_0} \rangle$	0.0114	0.0097	0.0038	0.0052	0.0039	-	-
A_0	10.9019	10.9134	11.0328	11.0005	11.0668	-	11.05232[d]
B_0	0.4436	0.4668	0.4674	0.4718	0.4772	-	0.47697[d]
C_0	0.4258	0.4476	0.4482	0.4524	0.4565	-	0.45619[d]
$\langle \varepsilon_R \rangle$	0.01792	0.01672	0.00390	0.00795	0.00082	-	-
[a]Ref. [26]; [b]Ref. [3]; [c]Ref. [23]; [d]Ref. [31]							

Table IV. Comparison of selected spectroscopic constants for HOCl						
	CI	CI+Q	CI/SEC	CI+Q/SEC	KP	Expt.
α_1^A (MHz)	23127	22967	22964	25381	23593	23681^b
α_2^A (MHz)	-20057	-19822	-20496	-19995	-21135	-23637^b
α_3^A (MHz)	1010.4	980.8	1036.9	1030.0	903.2	935.1^b
α_1^B (MHz)	-6.14	10.85	11.09	25.36	21.29	21.98^b
α_2^B (MHz)	41.69	35.97	32.34	30.31	26.44	24.58^b
α_3^B (MHz)	149	138	137	129	133.9	138.0^b
α_1^C (MHz)	5.5	21.6	21.9	36.9	32.11	32.50^b
α_2^C (MHz)	75.18	70.06	67.01	65.23	61.91	61.97^b
α_3^C (MHz)	146.9	136.5	135.5	127.9	132.7	136.7^b
$\langle \varepsilon_\alpha \rangle$	0.3813	0.1866	0.1676	0.1145	0.0359	-
D_J (MHz)	0.02644	0.02607	0.02586	0.02570	0.02643	0.02691^a
D_{JK} (MHz)	1.15995	1.15237	1.14462	1.16416	1.2030	1.25312^a
D_K (MHz)	103.957	106.691	110.509	111.2934	113.99	129.959^a
$\langle \varepsilon_D \rangle$	0.0973	0.0969	0.0838	0.0865	0.0602	-
x_{11} (cm^{-1})	-81.57	-81.18	-84.45	-82.19	-84.74	-85.55^b
x_{22} (cm^{-1})	-3.51	-6.31	-6.75	-7.48	-7.78	-7.64^b
x_{33} (cm^{-1})	-5.19	-5.14	-5.23	-5.17	-4.76	-
x_{12} (cm^{-1})	-23.83	-25.91	-24.64	-30.08	-25.66	-26.16^b
x_{13} (cm^{-1})	16.52	6.04	4.04	-3.12	-1.48	-1.93^b
x_{23} (cm^{-1})	-12.30	-10.67	-10.38	-9.25	-8.62	-
$\langle \varepsilon_x \rangle$	0.2254	0.0780	0.0627	0.0702	0.0156	-
^{a}Ref. [24]; ^{b}Ref. [26].						

Table V. Comparison of calculated and experimental forcefields for HOCl. Units of the force constants are aJ $a_0^{-(n_1+n_2)}$ rad$^{-n_3}$.

(n_1, n_2, n_3)	CI	CI+Q	CI/SEC	CI+Q/SEC	KP	Expt. [30]
$(2,0,0)$	8.0414	7.9933	8.1558	8.0930	8.0706	8.1110
$(0,2,0)$	3.5774	3.6438	3.8349	3.8043	3.8880	3.878
$(0,0,2)$	0.8334	0.8322	0.8378	0.8322	0.8405	0.833
$(1,1,0)$	-0.1820	-0.1576	-0.1484	-0.1357	-0.1335	-0.166^*
$(1,0,1)$	0.0379	0.0406	0.0434	0.0455	0.0389	0.021^*
$(0,1,1)$	0.4687	0.4695	0.4863	0.4791	0.4928	0.503
$(3,0,0)$	-57.8076	-56.1609	-57.1909	-59.3468	-56.713	-57.41
$(0,3,0)$	-21.7410	-20.9169	-21.9026	-20.7369	-21.700	-22.10
$(0,0,3)$	-0.6699	-0.5849	-0.5975	-0.5135	-0.654	-0.7070
$(2,1,0)$	1.8677	$1.-344$	0.9803	0.3774	0.483	0.872
$(1,2,0)$	-0.7544	-0.4666	-0.5641	-0.3131	-0.248	-0.021^*
$(2,0,1)$	-0.5182	-0.2444	-0.2252	-0.0716	-0.088	0.045^*
$(0,2,1)$	-1.9807	-1.7184	-1.7064	-1.4851	-1.617	-1.685
$(1,1,1)$	-0.2753	-0.2364	-0.2247	-0.1942	-0.238	0.033^*
$(1,0,2)$	-0.1406	-0.1770	-0.1530	-0.2005	-0.161	-0.062^*
$(0,1,2)$	-1.1595	-1.0723	-1.0660	-1.0050	-1.007	-0.998
$(4,0,0)$	398.9549	366.3638	358.7093	426.6863	356.77	322.0
$(0,4,0)$	111.6494	92.8969	94.2437	77.3568	96.29	64.3^*
$(0,0,4)$	1.3199	0.1256	-0.0508	-0.4723	-0.37	-0.444
$\langle \varepsilon_f \rangle^{**}$	1.26	0.85	0.77	0.69	0.76	-

*Fixed to values determined at the MP3/DZP level.

**Only force constants for which experimental values are available are considered.