HOCl Ro-Vibrational Bound-State Calculations for Nonzero Total Angular Momentum[†]

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The Lanczos homogeneous filter diagonalization method has been employed to compute the HOCl ro-vibrational states for a range of total angular momenta ($J = 0$, 1, 5, 10, 11, 20, 30) on a newly developed ab initio potential energy surface by Nanbu et al. (*J. Theor. Comput. Chem.* **2002**, *1*, 263). For such computationally challenging calculations, a parallel computing strategy has been incorporated into our method to perform the matrix−vector multiplications. For the computed low bound states, a spectroscopic assignment has been made and the widely used approximate adiabatic rotation method has been tested for the broad range of total angular momenta for this deep-well system. Comparison of experimental results with exact quantum mechanical calculations for the selected far-infrared transitions involving the range of total angular momenta has been made possible for the first time.

1. Introduction

Paul M. Dirac stated in 1929 (shortly after the introduction of the Schrodinger equation) that “the fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws lead to equations that are too complex to be solved”. Seventy seven years later, the complete description of chemical reactions has been realized only for small molecular systems of 3−4 atoms. In the case of unimolecular systems, most such calculations have focused on the nonrotating case. Even for scattering calculations, exact results at $J = 0$ are often extrapolated to larger J via approximations. Exact nonzero total angular momentum ($J > 0$) calculations are essential, however, for a complete description of quantum reactive scattering, thermal kinetics, energy transfer, and also in correctly simulating molecular spectroscopy. This latter application provides the context of the present paper in which we explore the capabilities of recent methodological developments for exact quantum dynamical calculation of ro-vibrational bound states over a wide range of angular momenta for the challenging and important HOCl molecular system.

These $J > 0$ calculations are still very challenging even for triatomic reactions, especially when dealing with complex-forming systems. The major reason for this situation is the so-called “angular momentum catastrophe”:[1] many $J > 0$ calculations have to be performed, and the size of the Hamiltonian matrix increases linearly with J. For these nonzero J calculations, it is apparently impractical to employ conventional direct diagonalization methods because of the requirement of a large and often prohibitive computer core memory. Several sophisticated basis set contraction schemes[2,3] do exist, but because of their unfavorable scaling they are limited to optimized basis sets of $N < 10\,000$. Variational approaches can be used to compute the low bound states accurately, but for high-lying bound states, convergence becomes difficult with the increasing size of the basis set.[4,5] However, iterative methods such as the real Chebyshev iterative method[6−8] and the Lanczos method[9,10] are well suited to solving this large-scale eigenvalue problem (or, for reactive scattering, the linear system generated by the causal Green operator) and in recent years have become increasingly popular. These methods are useful, especially for large basis sets, because they do not require explicit storage of the Hamiltonian matrix. Rather, only the multiplication of the Hamiltonian onto a vector is required. When combined with a sparse representation of the Hamiltonian such as a discrete variable representation (DVR),[11] both memory and CPU time can be reduced dramatically.

Lanczos methods exploit the sparsity of the tridiagonal subspace Hamiltonian generated by the iterative Lanczos algorithm.[9] Although the Lanczos algorithm has been used commonly for matrix diagonalization[10] and short-time propagations,[12] recent work in the Brisbane lab has focused on exploring more general applications of the Lanczos representation, including spectral densities,[13−15] filter diagonalization for bound states and resonances,[16−21] partial resonance widths in unimolecular decay,[22] and state-to-state reactive scattering.[23,24] An important feature of these newer Lanczos implementations is that all physically relevant information is extracted from within the

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Lanczos representation. This allows a single Lanczos iteration of arbitrary length to be utilized for the propagation rather than a sequence of short iterations. We note that for scattering or resonance applications the absorbing boundary conditions are imposed within the Lanczos algorithm by incorporation of a complex absorbing potential (CAP) into the Hamiltonian. This has the consequence that the Lanczos iterations are complex and yield a complex-symmetric tridiagonal representation of the Hamiltonian. Significant progress has also been made recently in the search for a real Lanczos subspace method capable of computing state-to-state reactive scattering probabilities.[25−27] These new real Lanczos methods require no complex absorbing potential or damping operator.

The HOCl system is very important in atmospheric chemistry because of its involvement in the depletion of ozone in the stratosphere and hence has been studied extensively from both experimental and theoretical perspectives. It is considered to be a temporary reservoir of the chlorine atoms and has been detected by far-infrared emission techniques.[28] For this reason a lot of effort has been devoted to the spectroscopic study of HOCl in the microwave, far-infrared, and infrared regions of its spectrum. For example, the high-resolution far-infrared spectrum of HOCl has been reported for total angular momentum above 50 with K_a above 6.[29,30] However, even this seemingly simple system involving only three atoms turns out to be very difficult to model quantum mechanically for high J values. So far most of the calculations have focused on the $J = 0$ case because of obvious computational difficulties. Exact quantum calculations including Coriolis coupling have been reported only for $J = 1$ and 3.[31,32] The potential energy surfaces (PES) most used are those by Bowman et al.[33,34] and those by Schinke et al.[35] These high-quality ab initio PESs are scaled to achieve agreement with the extant spectroscopic data for $J = 0$. Very recently, a new global ab initio PESs for HOCl system has been developed by Nanbu et al.,[36] which is suitable for both spectroscopy and reaction dynamics investigations. The newer ab initio surface by Nanbu et al. is not scaled or adjusted to reproduce the available spectroscopic data. In the present study, we provide the first extensive bound-state calculations on this new surface in comparison with previous calculations and spectroscopic data at $J = 0$, as well as providing the first rigorous calculations for large values of the total angular momentum ranging up to 30.

The computational tasks are too heavy using a conventional single-processor algorithm for the high angular momentum cases studied in this work; hence, we adopt a parallel computing model. The reasons for employing parallel computing are twofold. On one hand, the CPU time required to compute bound states as well as resonances for this system is substantial, partly because of the deep potential well, which can support hundreds of bound states even for the $J = 0$ case, corresponding to the HOCl complex. As J increases, the number of bound states will increase with J, which makes the convergence even more difficult. On the other hand, the storage requirement of the potential matrix and overlapping integrals also increases linearly with J. Thus, with the typical memory available on current cluster machines (i.e., a few gigabytes per node), the employment of parallel computing strategies becomes unavoidable for higher J values. Recently, several groups have begun to exploit the power of parallel computing in performing the rigorous $J > 0$ quantum calculations in TD wave packet methods and in sequential diagonalization and truncation methods.[37,38] In this paper, we show how such parallel computations make it possible to compute the dense ro-vibrational state manifold with computational times and storage requirements comparable to the $J = 0$ case. Our specific implementation involves a message-passing interface (MPI)[39] inserted in our local Fortran programs utilizing the Lanczos homogeneous filter diagonalization method.[20,22]

Because of the computational challenges of the exact calculations, approximate quantum methods such as adiabatic rotation (AR),[40] J-shifting,[41] and helicity conserving (HC)[42] or centrifugal sudden (CS) approximations are used commonly for nonzero J calculations. For the HOCl system, several groups have performed such approximate quantum calculations.[31,43−47] For example, Bowman et al.[31] have performed calculations for the $J = 1$ case using AR as well as CS approximation. Schinke at al.[43] and Bian and Poirier[44] have performed $J > 0$ calculations for selected resonances by ignoring the Coriolis coupling and by choosing $\Omega = 0$ (Ω is the body-fixed angular momentum projection quantum number). Nakamura et al. have investigated the validity of the J-shifting approximation for the O + HCl reaction and proposed an extended J-shift approximation.[46,47] As important as exact quantum methods may be, approximations may become unavoidable for complex and/or large systems. Therefore, it will be interesting to compare the exact quantum results with those from different approximate methods for a range of total angular momentum. The key issue in these approximations is whether a reasonably good quantum number, Ω, associated with the projection of total angular momentum on a body-fixed axis, exists. If the substates Ω of the wave function for $J > 0$ are coupled heavily, then the Coriolis coupling between the states cannot be ignored and any attempts to assign the helicity quantum number, Ω, will fail. We will examine this issue by comparing the exact quantum results with a rationally implemented AR approximation and a helicity quantum number Ω assignment for both spectroscopic symmetry calculations of bound states.

The rest of this article proceeds as follows. In Section 2 we describe the theoretical methods needed to characterize bound states for nonzero total angular momentum, together with a brief overview of our parallel computing model and some HOCl system-specific details. In Section 3 we present the results of $J = 0$, 1, 5, 10, 11, 20, and 30 bound-state calculations performed on the Nanbu et al.'s potential energy surface. Detailed comparisons with previous work for the low bound-state manifold as well as the comparisons with AR approximation and with experiments will also be given in Section 3. Section 4 concludes.

2. Methodology

In general, we treat the three internal Jacobi coordinates (R, r, γ) in discrete variable representation (DVR), whereas the three Eulerian angles (θ, ϕ, ψ) are described in a basis set.[48−50] This procedure is very efficient because the potential part of the Hamiltonian matrix is diagonal, which can reduce the memory requirement substantially. The triatomic Hamiltonian in Jacobi coordinates in a body-fixed frame is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R - \frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{l}^2}{2\mu R^2} + \frac{\hat{j}^2}{2\mu r^2} + V(R, r, \gamma) \quad (1)$$

where orbital angular momentum, $\hat{l}^2 = (\hat{J} - \hat{j})^2 = \hat{J}^2 + \hat{j}^2 - 2\hat{J}\cdot\hat{j}$. Using symmetry-adapted symmetric top eigenfunctions to expand the total wave function, one can get the coupled equations

$$\hat{H}_{\Omega,\Omega} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R - \frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + V(R, r, \gamma) + \left(\frac{1}{2\mu R^2} + \frac{1}{2\mu r^2}\right)\left(-\frac{\hbar^2}{\sin\gamma}\frac{\partial}{\partial\gamma}\sin\gamma\frac{\partial}{\partial\gamma} + \frac{\hbar^2\Omega^2}{\sin^2\gamma}\right) + \frac{\hbar^2}{2\mu R^2}[J(J+1) - 2\Omega^2] \quad (2)$$

and

$$\hat{H}_{\Omega,\Omega\pm1} = (1 + \delta_{\Omega},m)^{1/2}\frac{\hbar^2}{2\mu R^2}\sqrt{J(J+1) - \Omega(\Omega\pm1)}\left[\pm\frac{\partial}{\partial\gamma} + (\Omega\pm1)\cot\gamma\right] \quad (3)$$

with $m = 0$ for $\hat{H}_{\Omega,\Omega+1}$ and $m = 1$ for $\hat{H}_{\Omega,\Omega-1}$. Such coupled equations can be represented in DVR

$$H_{\lambda\Omega}^{\lambda'\Omega'} = -\frac{\hbar^2 1}{2\mu R}\frac{\partial^2}{\partial R^2}R\delta_{\lambda'\lambda}\delta_{\Omega'\Omega} - \frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r\delta_{\lambda'\lambda}\delta_{\Omega'\Omega} + V(R, r, \gamma_\lambda^\Omega)\delta_{\Omega'\Omega} + \left(\frac{1}{2\mu R^2} + \frac{1}{2\mu r^2}\right)\sum_j T_{j\lambda}^\Omega[j(j + 1)\hbar^2]T_{j\lambda'}^\Omega\delta_{\Omega'\Omega} + \frac{\hbar^2}{2\mu R^2}[J(J+1) - 2\Omega^2]\delta_{\lambda'\lambda}\delta_{\Omega'\Omega} + \sum_j T_{j\lambda}^\Omega\, t_{\Omega,\Omega+1}^{J_j}\, T_{j\lambda'}^{\Omega+1}\delta_{\Omega'\Omega} + 1 + \sum_j T_{j\lambda}^\Omega\, t_{\Omega,\Omega-1}^{J_j}\, T_{j\lambda'}^{\Omega-1}\delta_{\Omega'\Omega-1} \quad (4)$$

with $t_{\Omega,\Omega\pm1}^{J_j} = -(1 + \delta_{\Omega,m})^{1/2}\ (\hbar^2/2\mu R^2)\sqrt{J(J+1)-\Omega(\Omega\pm1)}\sqrt{j(j+1)-\Omega(\Omega\pm1)}$.

In eq 4, we have used Ω-dependent DVR for the γ coordinate, which is obtained by diagonalizing the coordinate operator ($x = \cos\gamma$) matrix ${}^{\Omega,\gamma}\Delta_{jj'} = \int_{-1}^{1} \Theta_j^\Omega(\gamma)\ x\Theta_{j'}^\Omega(\gamma)\ dx$. Here $\Theta_j^\Omega(\gamma)$ is the associated Legendre polynomial. In the direct diagonalization scheme, the DVR points and the transformation matrix are simply the eigenvalues and the eigenvector matrix of the coordinate operator matrix. For R and r coordinates, we have used potential optimized DVR.[51] The details of the DVRs will be given in section 3.

In Lanczos iteration, we choose a normalized, randomly generated initial vector, $v_1 \neq 0$, and set $\beta_1 = 0$ and $v_0 = 0$. Then use the basic Lanczos algorithm for complex-symmetric matrices[52]

$$\beta_{k+1}v_{k+1} = \hat{H}'v_k - \alpha_k v_k - \beta_k v_{k-1} \quad (5)$$

to project the non-Hermitian absorbing potential augmented Hamiltonian into a Krylov subspace. The $M \times M$ tridiagonal representation of the Hamiltonian, T_M, has diagonal elements, $\alpha_k = (v_k|\hat{H}'|v_k)$, and subdiagonal elements, $\beta_k = (v_{k-1}|\hat{H}'|v_k)$. Note that a complex-symmetric inner product is used (i.e., bra vectors are not complex conjugated). The two vectors, $\{\alpha\}$ and $\{\beta\}$, are stored in Lanczos iterations for later FD analysis to extract physical information such as bound-state or resonance quantities.

Though conceptionally simple, the propagation is the most time-consuming part of the calculation. We use MPI to perform parallel computation for the matrix−vector multiplications. For even spectroscopic symmetry, the 4D matrix−vector multiplication looks like

$$\begin{pmatrix} H_{00} & H_{01} & 0 & 0 \\ H_{10} & H_{11} & H_{12} & 0 \\ 0 & H_{21} & H_{22} & \dots \\ 0 & 0 & \dots & \dots \end{pmatrix}\begin{pmatrix} \psi_{\Omega=0} \\ \psi_{\Omega=1} \\ \psi_{\Omega=2} \\ \vdots \end{pmatrix} = \begin{pmatrix} \phi_{\Omega=0} \\ \phi_{\Omega=1} \\ \phi_{\Omega=2} \\ \vdots \end{pmatrix} \quad (6)$$

with, $\phi_\Omega = H_{\Omega,\Omega-1}\psi_{\Omega-1} + H_{\Omega,\Omega}\psi_\Omega + H_{\Omega,\Omega} + 1\psi_{\Omega+1}$. For odd spectroscopic symmetry, the Hamiltonian matrix is the same except, $\Omega = 1, 2, ..., J$. The spectroscopic symmetry parity is defined as $(-1)^{J+p}$, with p being the parity of the wave function under inversion of the space-fixed nuclear coordinates. We adopt a natural way to distribute the problem with respect to Ω block, which will make the calculations of $\{\alpha\}$ and $\{\beta\}$ much easier and the modifications of our code as few as possible for parallel computing. We assign one processor as master processor (ID $= 0$), which is used to write $\{\alpha\}$ and $\{\beta\}$, and assign all other processors as working processors, which are used to perform the matrix−vector multiplications for different Ω components. Our implementation has the flexibility that any number of cpus ($2 \le n \le J + 2$) can be employed in our Sun cluster machine. According to the Coriolis coupling rules, only two nearest neighboring Ω components need to communicate and we use the MPI_SEND and MPI_RECEIVE commands to carry out such communications. In this way the data transfer between processors is not too heavy. We distribute the work load as equally as possible over processors. However, because $j_{\min}$ is different for each Ω component, but $j_{\max}$ is the same, that is, the DVR size for γ is different for each Ω component, and also for the highest or the lowest Ω components, only one Coriolis coupling term is required; thus, the load for each processor is still not well balanced. Indeed, in distributed computing, there is always a tradeoff between load balance and the complications in coding. Our principle is that strict balancing is not required, but the algorithm we have implemented works well generally regardless.

We note that other parallel models have been used to calculate ro-vibrational states. For example, Wu and Hayes[53] defined a conceptual 3D mesh where Ω is used as one of the indices, Mussa and Tennyson[38] have employed a two step procedure, and Eggert et al.[54] described a fine granularity parallel Lanczos calculation in which a pseudo spectral split Hamiltonian scheme has been employed to implement the acting of the Hamiltonian on the wave function. Here different parallel strategies are employed to suit different methods and also the different machine architectures.

Finally, we perform filter diagonalization inside the subspace representation to extract the bound and (when required) resonance information for any chosen energy windows. The key issue in LHFD is to solve the homogeneous linear system by using an efficient backward three-term substitution recursion. The details of LHFD have been given in refs 20 and 22.

2.1. HOCl System Specifics. The triatomic HOCl Hamiltonian matrix was set up in terms of reactant Jacobi coordinates, and the ab initio potential energy surface developed recently by Nanbu et al.[36] was employed. For the two radial coordinates, a potential-optimized DVR[51] (PODVR) was utilized to reduce the size of the Hamiltonian matrix. For the R coordinate, we have used $N_R = 130$ PODVR points, which were contracted from 360 evenly spaced primitive sinc DVR points[55] spanning the range from 2.0 a_0 to 12.0 a_0 with the one-dimensional reference potential, $V(R, r_e, \theta_e)$. Similarly, for the r coordinate, $N_r = 80$ PODVR points were obtained from 245 primary DVR points spanning the range from 1.0 a_0 to 6.0 a_0 using the reference potential, $V(R_e, r, \theta_e)$. For the γ variable, Ω-dependent DVR functions, defined by correspondingly associated Gauss-Jacobi quadrature points, were employed. The spectroscopic symmetry originated from the Wigner D-functions has also been considered. The resulting direct product basis set was further contracted by discarding those points whose potential energies were higher than the cutoff energy, $V_{\mathrm{cutoff}} = 0.48$ eV (here the zero energy point is referred to as the dissociation limit of O(^{1}D) + HCl channel), resulting in the final basis size of approximately, 294 097 × (J + 1), for even spectroscopic symmetry and approximately, 294 097 × J, for odd spectroscopic symmetry.

In our calculations the Lanczos propagations and FD analysis are completely separated. Although parallel computations are employed only in the propagation step, the FD analyses are performed using conventional nonparallel architectures. Because of the communications and loading balance issues mentioned above, the parallel computing model does not scale ideally with (J + 1) for even spectroscopic symmetry or J for odd spectroscopic symmetry. However, one can achieve wall clock times (e.g., for even symmetry $J = 5$ HOCl case) that are within about a factor of 2 of $J = 0$ calculations (for the same iteration numbers). For nonparallel computing, the wall clock times will approximately be a factor of 6 of $J = 0$ calculations. In our calculations, 2 cpus have been used for both even and odd spectroscopic symmetries for the $J = 1$ case, 4 cpus have been used for both even and odd spectroscopic symmetries for the $J = 5$ case, and 8 cpus have been used for both even and odd spectroscopic symmetries for the $J = 10$, 11, 20, and 30 cases.

3. Results

We have employed the LHFD method summarized above to compute the low-lying ro-vibrational bound-state manifold of the HOCl molecule at $J = 0$, 1, 5, 10, 11, 20, and 30 for both spectroscopic symmetries. To facilitate the comparisons with previous reported calculations and with the experimental results, in the following tables the calculated energies are shifted such that the zero energy point is referred to as the ground-state energy of HOCl for $J = 0$, which is −4.009613 eV relative to the O(^{1}D) + HCl dissociation limit. For the $J = 0$ case 2000 Lanczos iterations are sufficient to converge the lowest 20 bound states, while for the $J = 30$ case 10 000 Lanczos iterations are sufficient to generate the results reported herein. In Table 1 we have listed the 20 lowest bound-state energies from $J = 0$ calculations for comparison. In this table, the second column contains the spectroscopic assignments of the states with ν_1, ν_2, and ν_3 being the number of quanta in the OH stretching, HOCl bending, and OCl stretching local modes, respectively. The third column contains the results calculated with the present quantum LHFD method, while the fourth column provides the reported results from Bowman et al.[31] The last column gives the available spectroscopic data.[30,56−59] Inspection of the energies shows that they are in general agreement, but because of different PESs and/or different methods employed, the differences for some bound states are still relatively large. It is important to stress again at this point that the PES of Nanbu et al. we employ in this paper is a genuine ab initio surface, without being scaled and/or being inverted to reproduce the 22 available experimental vibrational bound-state energies, as was done previously for the other two high quality ab initio PESs.[34,35] Another technical point is that spline interpolation of potential energies at grid points has been employed in this PES, whereas in the other two PESs fitted analytical expansions have been employed. We have checked one-dimensional reference potentials $V(R, r_e, \theta_e)$ and $V(R_e, r, \theta_e)$, generated on both the primary grids and the optimized grids. The interpolated surfaces display some irregularities, indicating the possibility of artificial errors due to insufficient ab initio data points. This may explain why the reported vibrational state energies are not as accurate as the previous calculations and the experimental ones, despite the high level of the ab initio calculations. Further work is underway to explore this issue and develop the global ab initio potential energy surface to give a better representation of the minimum because it has been developed and tested initially with a view to reactive scattering calculations. However, as will be seen below, the present PES suffices for the purposes of this paper, which explores the exact quantum dynamical calculation of the rotational progressions to high J.

TABLE 1: Vibrational Energies of the First 20 Bound States at $J = 0$[a]

n	(ν_1, ν_2, ν_3)	this work	Bowman	experimental
1	0, 0, 0	0.00	0.000	
2	0, 0, 1	650.58	724.336	724.36
3	0, 1, 0	1261.97	1238.617	1238.62
4	0, 0, 2	1309.21	1444.107	1438.68
5	0, 1, 1	1926.92	1953.748	
6	0, 0, 3	1963.22	2154.028	
7	0, 2, 0	2522.28	2456.363	2461.21
8	0, 1, 2	2592.00	2663.255	
9	0, 0, 4	2615.53	2852.172	
10	0, 2, 1	3185.19	3163.826	
11	0, 1, 3	3245.26	3362.256	
12	0, 0, 5	3268.65	3537.056	
13	1, 0, 0	3599.72	3609.972	3609.48
14	0, 3, 0	3792.41	3670.391	3668.44
15	0, 2, 2	3846.33	3865.881	
16	0, 1, 4	3888.63	4049.231	
17	0, 0, 6	3921.39	4208.750	
18	1, 0, 1	4225.06	4333.990	4331.91
19	0, 3, 1	4441.93	4368.682	
20	0, 2, 3	4500.65	4556.721	

[a] The ro-vibrational ground-state energy was calculated at −4.009613 eV relative to the O(^{1}D) + HCl dissociation limit, which is referred to as the zero energy point. All energy units are in cm^{-1} and quantum numbers (ν_1,ν_2,ν_3) are used to label the energy levels. See the text for more details.

In Supporting Information Tables 2−7, we report the low-lying ro-vibrational bound-state manifold for nonzero total angular momentum values $J = 1$, 5, 10, 11, 20, and 30. For the high J values, the exact quantum calculations including Coriolis coupling terms are still very challenging even though the total number of Lanczos iterations is modest (ca. 10 000) because of the ever increasing size of the basis set. For instance, it takes one week of wall time to converge the reported low-lying bound-state energies for $J = 30$ using 8 cpus (4 nodes) of an Opteron dual-processor 2.2 GHz grid. Without the combination of parallel computing with the more advanced methodology, it would be exceedingly difficult if not prohibitive to perform these benchmark test calculations. In these tables the calculated bound states can be assigned in terms of the three fundamentals ν_1, ν_2, and ν_3 and in terms of J, K_a, and K_c. Here quantum numbers K_a and K_c are used to label the energy levels using the rigid rotor approximation because HOCl is nearly a symmetric top (K_a is indeed the same as Ω).

To test the adiabatic rotation approximations for such a range of J values, we have performed the approximation calculations using Bowman et al.'s adiabatic rotation method[60] for the low bound-state energies (J-shifting and adiabatic rotation approximations are at the same level of approximations, with the former being employed in scattering calculations and the latter being used in ro-vibrational state calculations). Rotation constants A, B, and C used in this work are taken from experimental results,[30] for example, (20.46360936, 0.504277847, 0.491162955) for the (0,0,0) band, (20.43372436, 0.499681662, 0.486602466) for the (0,0,1) band, and (21.22679572, 0.503461812, 0.489043678) for the (0,1,0) band (unit in cm^{-1}). Comparing of the quantum and AR results in the Tables 2−7 one can see how the AR approximation performs when J and K_a vary. For low J values, the performance of the AR approximation is excellent. For example, for $J = 1$ case, there is little difference between the quantum and AR results. Then as J increases, the results from AR approximation start to deviate from the exact quantum results, but even up to $J = 30$ the AR approximation still predicts reasonable results. In terms of quantum number K_a, the AR approximation will become worse as K_a increases. This can be seen through the inspection of the quantum and AR results in the same vibrational band for each $J > 0$ table. These results indicate that the mixing of different Ω components of the wave function for $J > 0$ is not apparent, and AR results are indeed very close to the exact quantum results, at least for the low energy part. Given that there are errors in the vibrational energy levels based on pure ab initio PES and that in AR approximation we have used the experimental rotational constants A, B, and C in this work, the agreement is indeed quite satisfactory.

Another more complicated approximation that is widely used in dynamical calculations is the so-called helicity conserving approximation (also known as centrifugal sudden approximation).[61,62] In the helicity conserving (HC) approximation, the Coriolis coupling blocks $\hat{H}_{\Omega,\Omega\pm1}$ in eq 3 are simply ignored and the diagonal block $\hat{H}_{\Omega,\Omega}$ in eq 2 can be solved independently for each Ω at a fixed J value. A common characteristic in these different levels of approximations is whether a good quantum number Ω exists. In this paper we do not perform helicity conserving calculations explicitly, instead we will make a relatively easy comparison of the energy levels with the same K_a but from different spectroscopic symmetries, to see whether Ω is a good quantum number; thus, we can judge whether helicity conserving approximation is a good approximation. If the calculated energies from even and odd symmetries are nearly the same for the same Ω component, then Ω is a good quantum number. This is because there exists near degeneracy for the same Ω components from both symmetries. Therefore, helicity conserving calculations or even the much simpler adiabatic rotation approximations should be accurate, which will save quite a lot of computational time. By such comparison of the corresponding energy levels we can see that for the HOCl system there does exist near degeneracy for the same Ω components from both symmetries, indicating that Ω is indeed a good quantum number. We also note that whenever the energy levels become close, for example, the first two energy levels in each band, the mixing of different Ω components is more serious, and the differences of the corresponding energy levels become relatively large. The above observations indicate that for the HOCl system, at least for the low-energy part of the spectrum, the Coriolis coupling is generally not very important and various approximations can be used to predict approximately the ro-vibrational energies.

Having calculated the ro-vibrational energies and assigned them, it is straightforward now to compare the high-resolution experimental far-infrared transitions[29] with our computed ones. In Table 8 we have listed selected 56 such transitions involving $J = 5$, 10, 11, 20, and 30 for the two lowest vibrational bands. The listed experimental results have been reported 15 years ago by Carlotti et al. (see the fifth column).[29] Because of the obvious computational difficulties, exact quantum calculations have hitherto not been possible. Comparison of the observed and computed transitions indicates that the differences for all of the transitions are between 0.5 and 3 cm^{-1}. Such an agreement is unexpected at first, given that the PES used in this work does not predict the 22 known experimental vibrational state energies at $J = 0$ with such accuracy. However, after analysis we find that all of these transitions are pure rotational transitions (i.e., within the same vibrational band); hence, the inaccuracies in band origins caused by the PES can be approximately canceled for these far-infrared transitions. It seems that the accuracy of

TABLE 8: Comparison of Experiments and Quantum Calculations for Selected Far-Infrared Transitions[a]

n	(J', K_a, K_c)	(J'', K_a, K_c)	(ν_1, ν_2, ν_3)	OBS	CAL
1	11, 1, 11	10, 0, 10	0, 0, 0	30.47268	30.00
2	10, 2, 8	11, 1, 11	0, 0, 0	49.30875	48.59
3	30, 2, 28	30, 1, 29	0, 0, 0	56.94863	55.88
4	20, 2, 18	20, 1, 19	0, 0, 0	58.46497	57.55
5	11, 2, 9	11, 1, 10	0, 0, 0	59.39131	58.50
6	10, 2, 8	10, 1, 9	0, 0, 0	59.46407	58.57
7	5, 2, 4	5, 1, 5	0, 0, 0	59.92694	59.03
8	10, 2, 9	10, 1, 10	0, 0, 0	60.17781	59.28
9	11, 2, 10	11, 1, 11	0, 0, 0	60.24701	59.34
10	20, 2, 19	20, 1, 20	0, 0, 0	61.15034	60.27
11	30, 2, 29	30, 1, 30	0, 0, 0	62.75077	61.99
12	11, 2, 10	10, 1, 9	0, 0, 0	70.40212	69.32
13	11, 2, 9	10, 1, 10	0, 0, 0	71.12366	70.03
14	10, 3, 8	11, 2, 9	0, 0, 0	88.58254	87.30
15	10, 3, 7	11, 2, 10	0, 0, 0	88.58710	87.30
16	30, 3, 27	30, 2, 28	0, 0, 0	99.19930	97.91
17	11, 3, 9	10, 2, 8	0, 0, 0	110.46226	108.79
18	11, 3, 8	10, 2, 9	0, 0, 0	110.46455	108.79
19	10, 4, 7	11, 3, 8	0, 0, 0	128.04666	126.19
20	10, 4, 6	11, 3, 9	0, 0, 0	128.04666	126.19
21	11, 4, 7	10, 3, 8	0, 0, 0	149.91366	147.67
22	11, 4, 8	10, 3, 7	0, 0, 0	149.91366	147.67
23	10, 5, 5	11, 4, 8	0, 0, 0	167.16715	164.76
24	10, 5, 6	11, 4, 7	0, 0, 0	167.16715	164.76
25	30, 5, 25	30, 4, 26	0, 0, 0	177.79184	175.14
26	30, 5, 26	30, 4, 27	0, 0, 0	177.79184	175.14
27	20, 5, 16	20, 4, 17	0, 0, 0	177.98236	175.37
28	20, 5, 15	20, 4, 16	0, 0, 0	177.98236	175.37
29	11, 5, 6	10, 4, 7	0, 0, 0	189.01961	186.28
30	11, 5, 7	10, 4, 6	0, 0, 0	189.01961	186.28
31	10, 6, 5	11, 5, 6	0, 0, 0	205.86410	202.93
32	10, 6, 4	11, 5, 7	0, 0, 0	205.86410	202.93
33	10, 2, 8	11, 1, 11	0, 0, 1	49.33260	48.93
34	20, 2, 18	20, 1, 19	0, 0, 1	58.39383	57.84
35	10, 2, 9	10, 1, 10	0, 0, 1	60.10094	59.58
36	11, 2, 10	11, 1, 11	0, 0, 1	60.16989	59.65
37	20, 2, 19	20, 1, 20	0, 0, 1	61.07015	60.57
38	30, 2, 29	30, 1, 30	0, 0, 1	62.66476	62.29
39	11, 2, 10	10, 1, 9	0, 0, 1	70.22696	69.59
40	20, 3, 17	20, 2, 18	0, 0, 1	99.30556	98.48
41	20, 3, 18	20, 2, 19	0, 0, 1	99.35080	98.43
42	11, 3, 9	10, 2, 8	0, 0, 1	110.23551	109.25
43	11, 3, 8	10, 2, 9	0, 0, 1	110.23880	109.25
44	10, 4, 7	11, 3, 8	0, 0, 1	127.97162	126.89
45	10, 4, 6	11, 3, 9	0, 0, 1	127.97162	126.89
46	20, 4, 16	20, 3, 17	0, 0, 1	138.71705	137.49
47	20, 4, 17	20, 3, 18	0, 0, 1	138.71705	137.49
48	11, 4, 7	10, 3, 8	0, 0, 1	149.63802	148.29
49	11, 4, 8	10, 3, 7	0, 0, 1	149.63802	148.31
50	10, 5, 6	11, 4, 7	0, 0, 1	167.04307	165.65
51	10, 5, 5	11, 4, 8	0, 0, 1	167.04307	165.63
52	30, 5, 25	30, 4, 26	0, 0, 1	177.56931	175.97
53	30, 5, 26	30, 4, 27	0, 0, 1	177.56931	175.97
54	20, 5, 15	20, 4, 16	0, 0, 1	177.75930	176.21
55	11, 5, 6	10, 4, 7	0, 0, 1	188.69489	187.03
56	11, 5, 7	10, 4, 6	0, 0, 1	188.69489	187.03

[a] Units are in cm^{-1}. See the text for more details.

the PES mainly affects the band origin, whereas the quantum dynamics calculations will determine the pure rotational spectrum. This indicates that even though the purely ab initio PESs have not yet reached spectroscopic levels of accuracy for the calculation of the vibrational band origins, the exact quantum dynamics calculations are capable of very good accuracy for predicting rotational transitions. The measurements of the rotational transitions in the far infrared (IR) range have proved to be of great value in the measurement of stratospheric HOCl.[28,29] From these data, the altitude concentration profiles, including diurnal variation, can be obtained. Of course, the experimental measurements are not always easy because of the weak nature of some rotational transitions and the lack of some infrared transitions of sufficient strength in atmospheric window regions, coupled with the low concentration of HOCl. In this respect, theoretical predictions are complementary to the experimental measurements. Comparison of the experimental transitions with theoretical predictions can help better understand the chlorine chemistry-based cycle that catalytically destroys ozone. In fact, this region of the far IR spectrum has proved valuable for a number of other stratospherically important molecules such as OH and HO_2 molecules.[28] Thus, the calculations made possible by the methodologies exemplified in this study of HOCl can find important applications.

4. Conclusions

In this paper the Lanczos homogeneous filter diagonalization (LHFD) method has been combined with a parallel computing strategy to calculate the challenging ro-vibrational bound-state manifold of HOCl at low energies with total angular momentum $J = 0$, 1, 5 10, 11, 20, and 30 using the ab initio PES of Nanbu et al. The widely used adiabatic rotation (AR) approximation has been tested against the exact quantum results for the range of total angular momenta. For the low-lying bound states, the results from quantum and AR methods are generally in good agreement. As J and K_a increase, the accuracy of the AR approximation can be seen to deteriorate, but still at the maximum value of J computed herein the performance is reasonable. Through analysis of the energy levels with the same K_a but from different spectroscopic symmetries, we can see that Ω is generally a good quantum number for the low-energy part of the bound-state manifold, implying that the helicity conserving approximation should be good. For the HOCl system, then, Coriolis coupling appears not to be as important as in other deep well systems such as in HO_2. Currently we are extending our calculations for HOCl to high-lying bound states and to resonances in order to further explore the performance of the approximate methods. Still higher values of the total angular momentum are of relevance for experimental studies and are also being investigated in our labs. Finally, further comparison of the results from the PES of Nanbe et al. with prior surfaces over a wide range of bound-state and scattering energies will also be important as a preliminary to full reactive scattering calculations on this important system.

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Supporting Information Available: Tables 2−7. This material is available free of charge via the Internet at http://pubs.acs.org.

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