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Citation: *The Journal of Chemical Physics* **121**, 4467 (2004); doi: 10.1063/1.1779577

View online: <http://dx.doi.org/10.1063/1.1779577>

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Accurate and highly efficient calculation of the highly excited pure OH stretching resonances of $O(^1D)HCl$, using a combination of methods

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(Received 6 May 2004; accepted 15 June 2004)

Accurate calculation of the energies and widths of the resonances of $HOCl$ —an important intermediate in the $O(^1D)HCl$ reactive system—poses a challenging benchmark for computational methods. The need for very large direct product basis sets, combined with an extremely high density of states, results in difficult convergence for iterative methods. A recent calculation of the highly excited OH stretch mode resonances using the filter diagonalization method, for example, required 462 000 basis functions, and 180 000 iterations. In contrast, using a combination of new methods, we are able to compute the same resonance states to higher accuracy with a basis less than half the size, using only a few hundred iterations—although the CPU cost per iteration is substantially greater. Similar performance enhancements are observed for calculations of the high-lying bound states, as reported in a previous paper [J. Theo. Comput. Chem. 2, 583 (2003)]. © 2004 American Institute of Physics. [DOI: 10.1063/1.1779577]

I. INTRODUCTION

It is well-known that local mode vibrations, and mode-specific features of molecules, are of great importance in bond-selective chemistry.^{1,2} Experimentally, the first successful example of bond-selective chemistry was observed in the HDO molecule,^{1–3} for which local mode overtone vibration of the OH stretch mode was realized. Mode-specific features are also found in $HOCl$, or hypochlorous acid, an important intermediate in the $O(^1D)HCl$ reactive system. Recent experimental studies of the J and K state-resolved dissociation of $HOCl$, excited to high OH overtones, reveal highly state-specific and mode-specific properties for this molecule. It is found that the dissociation rates deviate very substantially from the predictions of statistical theories such as RRKM,⁴ and in particular, the resonance states with many quanta in the OH stretch mode are particularly long-lived. Despite the small size of the molecule, this behavior is evidently due to slow intramolecular vibrational redistribution (IVR) in $HOCl$, owing to weak intramolecular coupling between the OH stretch mode and the other two degrees of freedom, when there is little to no excitation of the latter modes.

Following precedent,⁵ we denote the zeroth-order vibrational states in $HOCl$ as (ν_1, ν_2, ν_3) , where (ν_1) is associated with the O—H stretch mode, (ν_2) with the H—O—Cl bend, and (ν_3) with the O—Cl stretch. The unimolecular dissociation dynamics of $HOCl$ in the highly excited OH stretching states, i.e., $(\nu_1, 0, 0)$, have recently been investigated by Rizzo's group^{5–7} and Sinha's group^{8–10} using overtone-overtone double resonance spectroscopy. The technique enabled these groups to selectively deposit vibrational quanta into the OH stretch coordinate. The decay rate of the rovibrational $(6, 0, 0)$ resonance states, for many different J and K values, were carefully studied by both Callegari *et al.*⁶

and Dutton *et al.*⁸ However, this state does not appear as a resonance until $J \geq 19$.

In 2001, Callegari *et al.*⁵ extended the previous experimental investigations up to the $(7, 0, 0)$ and $(8, 0, 0)$ states, which exist as resonances down to $J = 0$. Their main findings are: (1) the $HOCl \rightarrow OH + Cl$ dissociation dynamics are not adequately described by statistical models—even for the $(8, 0, 0)$ state, which is around 5000 cm^{-1} above the dissociation threshold; (2) the average rate increases by about two orders of magnitude from $(6, 0, 0)$ to $(7, 0, 0)$ and another two orders of magnitude from $(7, 0, 0)$ to $(8, 0, 0)$; (3) the fluctuations of the resonance widths with rotational quantum number J , for $(7, 0, 0)$, are considerably less pronounced than for $(6, 0, 0)$, whereas a clear peak at $J = 15$ is observed for $(8, 0, 0)$.

The main purpose of this paper is to present an accurate and highly efficient calculation of the highly excited pure OH stretching resonance states of $HOCl$, with respect to both energies and widths (related to lifetimes, decay rates, etc.). Both the vibrational ($J = 0$) and rovibrational ($J > 0$) states are considered. This kind of calculation is quite challenging, since the vibrational $(8, 0, 0)$ state lies around $24\,200 \text{ cm}^{-1}$ above the ground state, $(0, 0, 0)$, and there are around 800 vibrational bound states lying below the $OH + Cl$ dissociation threshold. Moreover, close to and above the dissociation threshold, the density of states (in a numerical sense) is extremely high, and increases quickly with increasing energy. Iterative methods,^{11–29} such as are used here, are notoriously hard to converge at high energies, or when the density of states is otherwise large.^{30–32} Consequently, the $HOCl$ system serves as a useful benchmark for testing iterative methods under adverse conditions.

On the other hand, the particular iterative scheme used in this paper is by design very well suited to this kind of state-specific and mode-specific investigation. Regarding the former, the preconditioned inexact spectral transform (PIST)

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technique^{31–33} energetically selects out states in small groups, or even individually. Optimal separable basis plus Wyatt (OSBW) preconditioning^{18,22,30,34,35} drastically reduces the number of iterations required. To capture bond-selective features of particular vibrational modes, the phase space optimized discrete variable representation^{36–38} (PSO DVR) is used. Finally, complex absorbing potentials (CAPs) deal with the continuum aspects of the resonance calculation.^{39,40}

Besides displaying mode-specificity and state-specificity, HOCl is of great importance to the chemistry of the stratosphere and upper troposphere,^{41,42} and the reaction products OH, Cl, and OCl, resulting from HOCl photodissociation, are implicated in catalytic cycles participating in ozone depletion processes. Consequently, HOCl has attracted growing attention from both theorists and experimentalists.^{5,41–50} On the experimental side, there have been a number of studies on the spectroscopy^{51,52} and dissociation^{5–10} of HOCl.

On the theoretical front, several *ab initio* potential energy surfaces (PESs) for the O(¹D)HCl (or HOCl) system have been constructed, and several detailed dynamical calculations have been performed on the available PESs. As HOCl is an important intermediate in the O(¹D)+HCl reaction, a distinction is made between two kinds of PESs for the O(¹D)HCl system—one designed for O(¹D)+HCl reactive scattering studies, and the other for HOCl (HClO) spectroscopic and resonance studies. Of course, there are PESs which claim to be suitable for both kinds of investigation. As for the reactive scattering PESs,^{43,53–57} the first was published in 1984 by Schinke *et al.*⁴³ These PESs are for the ground, or 1¹A' electronic state. Recently, global *ab initio* PESs for the two excited electronic states, 1¹A'' and 2¹A', have been constructed by Nanbu *et al.*⁵⁸

The first PES of near-spectroscopic accuracy in the HOCl well region was constructed by Skokov, Peterson, and Bowman in 1998,⁴⁵ which we refer to as “SPB98.” SPB98 is a highly accurate semiglobal PES, computed using the MRCI+Q/CBS method; a year later, based upon SPB98, the same three authors constructed a more global *ab initio* PES which also correctly describes the HClO isomer.⁴⁶ For convenience, this PES is referred to as SPB99. To further improve the accuracy of SPB99, an adjustment was applied, using a perturbative inversion procedure to “exactly” reproduce the 22 known experimental bound vibrational energy levels, and the rotational constants for nine low-lying states, for HO³⁵Cl (*J*=0).⁴⁷ This corrected PES is the best available for the purpose of spectroscopic and resonance studies of HOCl; we refer to it as “Corrected SPB99.”

Recently, Weiss *et al.*^{59,60} have also published two high-quality semiglobal *ab initio* PESs, which are well suited to the study of HOCl spectroscopy and dissociation dynamics. The *ab initio* level of these PESs is comparable to that of SPB98 and SPB99, but they do not reproduce the experimentally known vibrational energies as well. Weiss *et al.*⁶⁰ also performed quantum mechanical calculations of the HOCl vibrational bound states on the Ref. 60 PES, using the filter diagonalization (FD) method.^{25–28} These authors provide a detailed analysis of the vibrational states.

Some detailed vibrational dynamical studies have been

previously performed on SPB98,^{61–63} SPB99,⁴⁶ and Corrected SPB99.^{49,50,64,65} Mussa *et al.*⁶³ and Skokov *et al.*⁶² performed some calculations for selected vibrational resonance states of HOCl (Refs. 62 and 63) using SPB98. Weiss *et al.*⁴⁹ performed large-scale dynamics calculations to investigate the unimolecular dissociation of the OH stretching states of HOCl, using the FD method and the Corrected SPB99 PES. Good agreement with the experimental resonance widths was obtained, and the main experimental observations,⁵ i.e., the tremendous increase of the dissociation rate from $\nu_1=6$ to 8 by about four orders of magnitude, were quantitatively reproduced. Zou *et al.*⁵⁰ calculated the vibrational resonance states of HOCl for the sixth and seventh overtones of the OH stretch, using a standard L^2 approach on the Corrected SPB99 PES.

Our group has also performed extensive dynamical calculations for the vibrational bound states of HOCl, using the Corrected SPB99 PES. This was the focus of a previous paper⁶⁶—referred to here as “Paper I.” In the present paper, calculations are performed for the (7,0,0) and (8,0,0) resonance states of HOCl, using the same Corrected SPB99 PES. Both vibrational and rovibrational states are considered, unlike the previous effort, for which only vibrational bound states were considered. The methodologies employed are similar, except that the resonance calculation requires the use of CAPs (Secs. II B and III B 3). The present work also differs from the previous investigation in that each calculation performed here is designed to compute the energy and width of a *single* resonance state only.

II. THEORETICAL CONSIDERATIONS

A. Phase space optimization and physical considerations

The starting point of any discrete variable representation (DVR) treatment is the “variational basis representation,”^{67–70} (VBR)—i.e., the eigenstates of some strongly separable approximate Hamiltonian $\hat{H}_0$, which is a sum of one-dimensional (1D) Hamiltonians, $\hat{H}_k = \hat{T}_k + V_k(\hat{q}_k)$. The potential-optimized (PO) DVR approach^{71,72} enables one to tailor the $V_k(q_k)$ to the particular system of interest, thus reducing the overall basis size, N , required to achieve a given level of accuracy in the computation—although the method does not specify how the effective potentials, $V_k(q_k)$, should be chosen, so as to minimize N .

Indeed, the standard choice of taking 1D “slices” of the PES through the equilibrium geometry can lead to disastrously inefficient results, as discussed in Paper I. It is not the PO DVR idea *per se* that is flawed; rather, it is the way that this is implemented via PES slices. To make headway, a more rigorous approach is required—one which derives the effective potentials using a true *optimization* procedure. The PSO DVR method achieves the desired goal, using a simple classical phase space picture that gives rise to nearly optimal $\hat{H}_k$'s.^{36–38}

In previous PSO DVR implementations, the “optimal” $\hat{H}_0$ was defined using the variational principle.³⁶ In practice, however, this is not the best approach, because it weights the highest and lowest computed eigenvalues equally. In Paper I,

a new optimization criterion was proposed that better reflects the actual numerical situation. The optimal $\hat{H}_0$ is now defined to be that which minimizes the value of N required to compute all eigenstates of $\hat{H}$ below some maximum energy of interest, $E_{\max}$. The optimal classical solutions are⁶⁶

$$H_k(q_k, p_k) = \min[H(q_1, p_1, \dots)]_{q_{j \neq k}, p_{j \neq k}}, \quad (1)$$

i.e., the minimum of $H(q_1, p_1, \dots)$ with respect to all but the k th phase space coordinates.

We now apply Eq. (1) to the three-atom vibrational problem in Jacobi coordinates, (r, R, γ) , where r is the separation between two of the atoms, R is the separation between the diatom center of mass and the third atom, and γ is the angle between the two Jacobi vectors. The results for the radial degrees of freedom are shown to be⁶⁶

$$H_r(r, p_r) = \frac{p_r^2}{2\mu} + \min[V(r, R, \gamma)]_{R, \gamma},$$

$$H_R(R, p_R) = \frac{p_R^2}{2m} + \min[V(r, R, \gamma)]_{r, \gamma}. \quad (2)$$

The γ situation is complicated; in the HOCl case, however, a nearly optimal substitute is⁶⁶

$$H_\gamma(\gamma, p_\gamma) = Ap_\gamma^2 + \min[V(r, R, \gamma)]_{r, R}, \quad (3)$$

where A is some effective value for $[1/(2\mu r^2) + 1/(2mR^2)]$. For instance, equilibrium values for r and R might be used, although this is rarely the best choice except at very low energies. A better approach (adopted here) is to use the phase space averaged value for A .^{37,66}

As discussed in Paper I, the minimal potential energy approach to generating $V_k(q_k)$ is fraught with several important caveats. One concerns the situation where the potential $V(q_1, \dots)$ has more than one local minimum with respect to the $q_{j \neq k}$, for fixed q_k . In general, the optimal solution of Eq. (1) is with respect to the *global* minimum. However, this may hop discontinuously from one local minimum to another, as the coordinate q_k is varied, which will result in a kink in the effective $V_k(q_k)$ curve, giving rise to less efficient DVRs.⁷³

On the other hand, PIST and other spectral window approaches are designed to compute only one state (or a small number of states) at a time. In keeping with this philosophy, a better approach is to restrict the minimization of the potential over just that region of configuration space which is relevant for the state(s) in question. The resultant effective potentials will thus give rise to basis sets that are tailor-made for the desired state(s). In the present HOCl context, this amounts to using the relevant *local* minimum to generate the $V_k(q_k)$ curve—even for q_k regions where this is no longer the *global* minimum. This procedure has the added advantage that the resultant $V_k(q_k)$ curves are free of kinks.

B. Complex absorbing potentials

The computation of resonance energies, and especially widths, poses certain special difficulties if finite basis representations are used. This has to do with the fact that resonances exist in the continuum, and are technically of infinite

extent, whereas finite matrix methods necessarily extend only over a finite region of configuration space. Sufficiently far from the interaction region, any given resonance behaves like a plane wave, suggesting that finite truncation of the configuration space grid should in principle be possible. In practice, however, any naive implementation of this idea gives rise to reflections off of the implicit hard wall at the grid edge, which then propagate unphysically back into the interaction region.

On the other hand, the above idea can be made to work, provided that the original Hamiltonian is modified so as to give rise to a complex-symmetric matrix representation. One then computes resonance energies and widths directly, as the real and imaginary parts of the matrix eigenvalues. Methods that operate in this fashion are known as “direct” methods.^{32,74,75} The two most important direct methods for computing resonances are the complex scaling method,^{76,77} and the CAP method.^{39,40} We make use of the latter, for which the original Hamiltonian is modified via the addition of the CAP, $-i\epsilon$. The effect of the CAP is to damp out outgoing flux, so that by the time it reaches the edge of the grid, there is very little probability left to be reflected back. This simple explanation is presented in time-dependent language, but is easily “translated” to the present time-independent context.

Note that in principle, issues of numerical instability may arise when iterative algorithms are applied to complex-symmetric matrices. In the particular case of the PIST method, the related issue of inexactness also comes into play. In practice, however, the CAP contribution is always so small that the matrices involved are nearly real-symmetric, and the convergence is anticipated to be numerically stable. This expectation is certainly borne out for the present investigation (Sec. IV); a more detailed, general discussion may be found in Ref. 32, particularly in the Appendix.

In any event, CAP methods have some important advantages: (1) there is no need to impose scattering boundary conditions on the solutions; (2) it is usually straightforward to determine energies and widths, even for very closely spaced and/or broad resonances. The latter property holds by virtue of the fact that different resonances correspond to distinct eigenvalues of the modified Hamiltonian matrix, although it should be stated that many nonresonance eigenvalues are also present. The primary disadvantage of CAPs is that they substantially increase the size of the basis or DVR grid needed to perform the calculation, along the direction of the dissociation coordinate (R , in the present case). This is because $\epsilon(R)$ may only be nonzero outside of the interaction region (in order not to interfere substantially with the correct dynamics), and moreover, requires a certain number of wavelengths over which to damp the outgoing wave.

There has therefore been a considerable effort in recent years to develop optimized CAPs, which require a minimal amount of space over which to operate. The present work uses an optimal 14th-order polynomial complex $\epsilon(R)$, with no linear term, as follows:^{78,79}

$$\begin{aligned}
\epsilon(R) &= AE_{\text{cap}}[2F(R) + iF(R)^2], \\
F(R) &= f\left(\frac{R-R_0}{R_{\text{max}}-R_0}\right), \\
f(z) &= 4.722\,07z^2 - 12.947\,23z^3 + 31.021\,50z^4 \\
&\quad - 58.475\,40z^5 + 96.364\,47z^6 - 134.785\,07z^7 \\
&\quad + 164.065\,66z^8 - 169.256\,33z^9 + 148.346\,31z^{10} \\
&\quad - 105.659\,65z^{11} + 59.971\,06z^{12} - 23.919\,28z^{13} \\
&\quad + 6.018\,63z^{14}.
\end{aligned} \tag{4}$$

In Eq. (4) above, E_{cap} is an estimate for the resonance energy along the dissociation coordinate, and A , R_0 , and R_{max} are convergence parameters. It is understood that $\epsilon(R)$ is non-zero only in the range $R_0 < R \leq R_{\text{max}}$.

III. NUMERICAL DETAILS

A. Overview

Resonance calculations were performed for HO^{35}Cl using the $1^1A'$ Corrected SPB99 PES.⁴⁷ The Hamiltonian is represented in Jacobi coordinates (r, R, γ) , as per Sec. II A, where r is the OH stretch, and $\gamma=0$ describes linear ClOH. In atomic units, the masses are as follows: $m_{\text{H}}=1837.152\,632\,7$; $m_{\text{O}}=29\,156.947\,092$; $m_{\text{Cl}}=63\,744.321\,041$.

The Hamiltonian matrix $\mathbf{H}$ was constructed from a PSO DVR basis, as described in Secs. II A and III B 1. The coordinate ranges used to generate the VBR are as follows:

$$\begin{aligned}
1.0 \leq r \leq 6.0 \text{ bohr}, \\
2.0 \leq R \leq 14.0 \text{ bohr}, \\
0 \leq \gamma \leq \pi.
\end{aligned} \tag{5}$$

Some calculations with coordinate ranges other than those reported above were also considered, but Eq. (5) was found necessary to obtain the high level of convergence reported in Sec. IV A. The coordinate ranges for r and γ are identical to those of the most accurate bound state calculations performed in Paper I; however, $R_{\text{max}}=14.0$ is somewhat larger, owing to the presence of the CAP.

Eigenvalues of $\mathbf{H}$ were computed using the PIST method, together with OSBW preconditioning (Sec. III C). PIST is a nested iterative technique for efficiently computing all eigenstates within a given spectral window, centered on the energy E . In effect, PIST applies the Lanczos algorithm⁸⁰ to the matrix $(E\mathbf{I} - \mathbf{H})^{-1}$, rather than to $\mathbf{H}$ itself, with the result that only a small number of Lanczos iterations, M , are required. Typically, $M \approx 3 \times$ the number of computed eigenvalues; however, the ratio for the number of computed resonance states is somewhat higher, as nonresonance eigenvalues are also computed.³²

For all of the calculations performed here, the Lanczos stopping criterion used is convergence of the desired resonance energy and width to 10^{-4} cm^{-1} or better. Each Lanczos iteration is itself implemented via an iterative linear solver, so that the total number of matrix-vector products, K , is around $K=ML$, where L is the average number of linear

solver iterations per Lanczos iteration. The linear solver algorithm utilized is QMR,⁸¹ with an (inexact) stopping parameter³¹ of 3.0×10^{-3} . The value of L is determined by the preconditioner used, in this case OSBW.

Although HOCl exhibits a range of different resonance behaviors, for purposes of the present paper, we are interested solely in the OH+Cl dissociation resonances corresponding to high excitations in the OH stretch. This application serves as an ideal test bed for the method used here, which as compared with other methods, is anticipated to be most efficient when small numbers of highly excited, mode-specific states are desired. The present application has just three such vibrational resonances: (7,0,0), (8,0,0), and (9,0,0). The first two will serve as the focus of the present work. The (9,0,0) case is not considered here, because the PES used is not expected to be valid in this energy regime (Sec. IV A).

For each of the two vibrational resonances considered, a completely separate calculation was performed. Thus, we are applying the “one-at-a-time” version of PIST (Paper I and Ref. 32) for the first time. In addition to the two vibrational resonance states, separate calculations were also conducted for the corresponding rovibrational resonances with $J>0$. For simplicity, and to enable comparisons with experiment and previous calculations, only the $K=0$ case is considered, for various J values up to $J=20$.

B. Potentials

1. Effective potentials for $J=0$

For the most part, minimum effective potentials were used, as per Sec. II A. However, the HOCl PES topography is rather complex, with a second local minimum for HClO (see Paper I), and various other features that complicate this basic strategy. For $V_r(r)$, the global minimum of $V(r, R, \gamma)$ with respect to R and γ (at fixed r), jumps discontinuously from the HOCl to the HClO local minimum, at around $r=3.15$ bohr. The latter is not important for the resonance states considered here; consequently, we adopt the strategy of Sec. II A, and continue to follow the HOCl local minimum up to $r_{\text{max}}=6.0$ bohr. This yields the smooth, solid curve of Fig. 1(a), which is used in all calculations performed here, and in Paper I.

For $V_R(R)$, there are three local minima; one for HOCl, one for HClO, and another for linear ClHO, which is the global minimum for sufficiently large R . The HClO minimum is once again ignored (even if it were included, there would be just a slight distortion of the $V_R(R)$ curve at intermediate R values). However, there is a small kink in $V_R(R)$ at $R=6.65$ bohr, where the HOCl and linear ClHO curves join together. At the crossing point, the potential value is $V_R(R)=0.090\,399$ hartree, whereas the two geometries are $(r=1.836, \gamma=1.570)$ and $(r=1.838, \gamma=3.142)$, respectively. The kink is barely perceptible in Fig. 1(b), and does not appear to cause any numerical difficulties. This potential is the same as that used in Paper I, except that it extends out to $R=14.0$ bohrs rather than $R=12.0$ bohrs.

For H_γ , we use Eq. (3), as justified in Paper I. The constant A was obtained from a phase space average of the

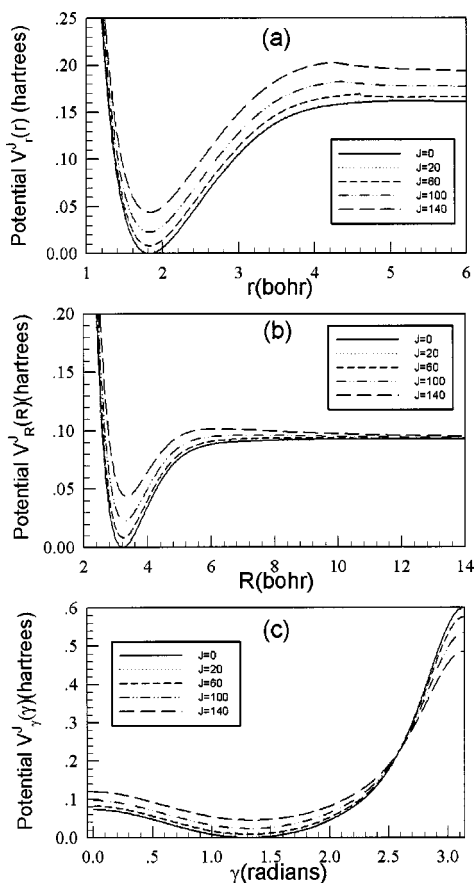


FIG. 1. Effective potentials for the HO³⁵Cl system in Jacobi coordinates (R, r, γ), and atomic units: (a) $V_r^J(r)$; (b) $V_R^J(R)$; (c) $V_\gamma^J(\gamma)$. Different values of J yield different potentials, as indicated in the legend.

classical Hamiltonian.³⁷ This led to the result $A = 0.000\,085\,967\,33$ (in atomic units). Although the minimal $V_\gamma(\gamma)$ curve is straightforward to obtain—especially the local minimum version, which would automatically avoid dissociation configurations (Sec. II A)—we have opted for an even more efficient customization of $V_\gamma(\gamma)$, based upon practical considerations. For the present resonance calculations, we are interested in the $(\nu_1, 0, 0)$ states, for which the energy in the HOCl bending mode is very small. Consequently, the system does not reach large γ values ($\gamma > 2.4$ corresponds to a very small H—O—Cl bend angle, whereas the equilibrium value for the latter is 102°).

According to the discussion in Sec. II A, we construct an improved $V_\gamma(\gamma)$ customized for calculations of the $(\nu_1, 0, 0)$ states, in the following way. For $0 \leq \gamma \leq \pi/2$, the minimal potential value is used. At $\gamma = \pi/2$, the minimal potential value is $0.006\,353\,04$ hartree, obtained for $R = 3.267\,36$ bohrs and $r = 1.82998$ bohrs. These radial values are then used to generate a “slice” potential for $V_\gamma(\gamma)$ in the $\pi/2 < \gamma \leq \pi$ range—i.e., $V_\gamma(\gamma) = V(1.829\,98, 3.267\,36, \gamma)$. The result is presented in Fig. 1(c), and is seen to be smooth in the vicinity of the join at $\gamma = \pi/2$. In any event, the modified $V_\gamma(\gamma)$ so obtained was found to be much more efficient for the resonance calculations performed here than was the unmodified potential.

2. Effective potentials for $J > 0$

Note that, strictly speaking, the above analysis applies only to the vibrational resonance calculations. For the $J > 0$ case, the true potential, $V(r, R, \gamma)$, should be replaced with a J -dependent “effective” potential (in the sense of angular momentum), $V^J(r, R, \gamma)$.^{18,82–84} Accordingly, the 1D effective potentials that results from Eqs. (2) and (3) should be J dependent. This is, in principle, very beneficial, from the standpoint of the present one-at-a-time computational philosophy, in that each of the $J > 0$ resonances would be computed using its own customized basis set.

On the other hand, the J dependence turns out to be very slight, over the J values considered here. Using $V^J(r, R, \gamma)$ as defined in Ref. 82, various J -dependent curves were computed, as presented in Figs. 1(a)–1(c). From the figures, it is clear that apart from an immaterial energy shift in the most relevant regions of configuration space, the curves are all very similar; for $J \leq 20$ in particular, the deviations are very slight indeed. Accordingly, the $J = 0$ effective potentials and basis sets were also utilized for all $J > 0$ calculations.

3. Complex absorbing potentials

In keeping with the philosophy of the present approach, the CAPs for the (7,0,0) and (8,0,0) calculations were converged separately. The energy values for E_{cap} were obtained as the differences between the (approximate) resonance energies, and the OH + Cl dissociation energy—where the latter is defined as the threshold for dissociation into OH($\nu = 0$) + Cl. This gives rise to respective E_{cap} values of $0.011\,108$ and $0.022\,254$ hartree.

Note that this presumes that all available energy is in the dissociation coordinate, which is of course incorrect, owing to the fact that the OH stretch is highly excited. This is accounted for by converging the calculation with respect to the strength parameter, A [Eq. (4)]. It is well-known that unless extremely high accuracy is desired, one may vary A by one or two orders of magnitude, without substantially changing the computed resonance eigenvalues, if all other parameters are converged. In fact, we conducted several convergence tests with A values between 0.2 and 3.0 , and found the variation to be substantially less than the desired accuracy. Accordingly, the value $A = 1.0$ was used in the final calculations.

Convergence tests were also applied for the remaining two parameters, R_0 and R_{max} , giving rise to the final converged values used here, $R_0 = 11.0$ and $R_{\text{max}} = 14.0$. Note that R_0 is a bit less than the $R_{\text{max}} = 12.0$ value needed for the bound state calculations of Paper I, as is expected for the present linear-free polynomial CAP.⁷⁹

C. Optimal separable basis plus Wyatt preconditioning

OSBW preconditioning is employed to reduce the number of QMR iterations, L , required per Lanczos iteration. Since $\mathbf{H}$ and the inverse preconditioner matrix are both sparse, the CPU cost of each QMR iteration matrix-vector product is small, although higher than it would be for a non-preconditioned calculation. In any event, OSBW was previously shown to reduce L by orders of magnitude in high-

TABLE I. PIST/OSBW parameters used in our calculations of the HO³⁵Cl resonances. The inexact QMR stopping parameter is 3×10^{-3} ; the Lanczos stopping criterion is convergence of the desired resonance (energy and width) to 10^{-4} cm⁻¹ or better. State label ν_1 refers to OH stretch mode. Basis set parameters are in terms of the three Jacobi coordinates R , r , and γ ; Wyatt parameters: window half-width (D); block size (W). Column VIII: number of Lanczos iterations (M). Last two columns: number of QMR iterations, average (per Lanczos iteration) and total.

Label	Window	Basis set parameters			Wyatt parameters		Iterations		
	Energy (hartrees)	Radial N_R	Radial N_r	Angular N_γ	D (hartrees)	W	Lanczos M	Average	Total
(7,0,0)	0.099 002	140	30	50	0.075	17 549	14	13.14	184
(8,0,0)	0.110 142	150	30	50	0.070	20 341	14	23.07	323
Weiss <i>et al.</i>		220	30	70					180 000

energy calculations^{31,32}—including that of the bound states of HOCl near the dissociation threshold (Paper I)—where all other standard preconditioners fail.^{18,22,30,33,85} One goal of the present work is thus to test the effectiveness of the OSBW preconditioner for the even more extreme task of computing HOCl resonances.

The first step in the construction of the OSB preconditioner is to partition the degrees of freedom into “inner” (fast) and “outer” (slow) categories. For technical reasons, γ must be an outer coordinate. Whereas previous implementations have tended to use both r and R as inner coordinates, for the HOCl system, it is better to treat R as the only inner coordinate (Paper I). Accordingly, all calculations reported here use R as the sole inner coordinate, and both r and γ as outer coordinates. Using this partitioning scheme, the bottleneck step of each QMR iteration scales as $N_R N_r^2 N_\gamma^2$, where N_R is the 1D PSO VBR basis size for R , etc.

The OSB preconditioner is greatly improved by combining it with a scheme due to Wyatt,³⁵ whereby coupling in the vicinity of the desired energy E is incorporated explicitly into the preconditioner. The coupling manifests as a diagonal block of matrix elements, which we term a “Wyatt block.” The number of iterations L decreases monotonically (and arbitrarily) with the size of the Wyatt block, which we denote W . Ideally, W is small compared to the total basis size, $N = N_R N_r N_\gamma$. In such cases, the overhead associated with the use of Wyatt preconditioning is negligible compared to the total CPU cost.

This was true of all previous OSBW applications, for which L was reduced to around three, regardless of the matrix size, energy, or density of states,^{31,32,66} thereby demonstrating *ideal scaling*^{31,32,66} (i.e., CPU cost per eigenvalue is independent of spectral location). For the highest energy bound state calculations of Paper I, however, we encountered a case where quite large W values were required. In any event, such eventualities require that an additional W^2 term be added to the CPU cost per iteration. A one-time LU decomposition of the Wyatt block, requiring $W^3/3$ operations, must also be considered. For large W , this can contribute significantly to the total CPU cost; the appropriate formula is thus

$$\text{No. of ops} = K(N_R N_r^2 N_\gamma^2 + W^2) + W^3/3. \quad (6)$$

IV. RESULTS AND DISCUSSION

A. $J=0$ calculation and convergence

Separate PIST calculations were performed for the two $J=0$ resonance states of interest. The central energies E for the two PIST resonance windows are 0.099 002 hartrees for the (7,0,0) state, and 0.110 142 hartree for the (8,0,0) state (Table I, Column II). Energies are relative to the (0,0,0) ground state for $J=0$, which has the energy of 2865.317 cm⁻¹ with respect to the classical minimum. For each calculation, only a *single* resonance state is desired. Note that since we do not know the resonance energies *a priori*, the central energies E do not correspond exactly to the desired resonance energies, but are merely estimates. Consequently, a few additional nonresonance eigenvalues, which are energetically near the desired resonance, are also computed with each calculation.

A variety of test calculations were performed to ensure the convergence of the computed results. First, we performed calculations using different ranges for R and r than those reported in Eq. (5). We found that an extended r range is very important for the convergence of states with high overtones in the OH stretching mode. In particular, these calculations reveal that the full range $1.0 \leq r \leq 6.0$ is absolutely necessary for achieving sub-wave-number accuracy; calculations using $r_{\max}=3.5$ or $r_{\max}=4.5$ lead to computed resonance energies that are around 5 cm⁻¹ too high. This is significant for Sec. IV C. In addition to the above parameters, and those already described in Sec. III, we also varied (separately for each resonance state) the basis truncation parameters N_R , N_r , and N_γ , as well as the Wyatt window half-width parameter D (which determines W ³¹). The converged parameters for each resonance window are presented in Table I.

To demonstrate the precision of the computed resonance energies and widths, we present some of the results for different basis sizes in Table II. The table indicates that the (7,0,0) resonance energies are converged to about 0.1 cm⁻¹, whereas the resonance widths are converged to about 0.0003 cm⁻¹. For the (8,0,0) resonance calculation, the convergence is not as high; the estimated errors are 0.2 and 0.3 cm⁻¹ for the computed energy and width, respectively.

Our $J=0$ calculational results for (7,0,0) and (8,0,0),

TABLE II. Comparison of the energies E and widths Γ for the vibrational ($\nu_1, 0, 0$) resonances of HO³⁵Cl, computed using different basis sets. The inexact QMR stopping parameter is 3×10^{-3} ; the Lanczos stopping criterion is convergence of the desired resonance (energy and width) to 10^{-4} cm⁻¹ or better. State label ν_1 refers to OH stretch mode. Basis set parameters are in terms of the three Jacobi coordinates R , r , and γ .

Window		Basis set parameters			Resonance energies and widths	
Label	Energy (hartrees)	Radial N_R	Radial N_r	Angular N_γ	E (cm ⁻¹)	Γ (cm ⁻¹)
(7,0,0)	0.099 002	140	30	50	21 725.56	2.68(−3)
		160	30	50	21 725.56	2.68(−3)
		160	30	60	21 725.56	2.40(−3)
		140	35	50	21 725.64	2.53(−3)
(8,0,0)	0.110 142	150	30	50	24 174.43	2.39
		140	30	50	24 174.48	2.36
		140	35	50	24 174.49	2.42
		140	30	60	24 174.60	2.66
		160	35	50	24 174.35	2.36

together with results from experiment⁵ and two previous calculations,^{49,50} are presented in Table III (all energies are relative to the zero point energy). All three of the calculations were performed on the same Corrected SPB99 PES,⁴⁷ presumably using the same masses, so the results should in principle agree exactly. However, the three calculations used very different numerical schemes. Weiss *et al.*⁴⁹ applied the filter diagonalization method in connection with a sparse DVR matrix representation, and a pure imaginary CAP, as described in Ref. 86; Zou *et al.*⁵⁰ used a customized L^2 basis from truncation recoupling, and a cubic pure imaginary CAP.

From Table III, we do indeed observe very good agreement among the three different calculations, especially for the resonance energies. For both the (7,0,0) and the (8,0,0) resonances, the computed energies agree to the level of accuracy reported in Refs. 49 and 50. As for the resonance widths, the (7,0,0) value computed here lies right in the middle (in a geometric sense) between the Weiss *et al.* and Zou *et al.* values—although the range of the computed widths is quite large, and well outside our converged error bars. There is better agreement among the computed widths for the (8,0,0) resonance, for which our computed width is the largest. Our result agrees with that of Weiss *et al.* to within the error bars, but does not agree with that of Zou *et al.*, which is substantially smaller. Generally speaking, the

differences between the three calculations are small, but in some cases [e.g., the (7,0,0) resonance width] quite significant relevant to the errors estimated from Table II; accordingly, we believe our calculations to be slightly more accurate.

Good agreement between the theoretical and experimental resonance widths is obtained, and the primary experimental observation⁵—i.e., the tremendous increase of the dissociation rate from $\nu_1 = 7$ to 8 by more than two orders of magnitude—is quantitatively reproduced. This stark behavior has been attributed to a combination of two features of the HOCl system:⁴⁹ (1) weak coupling between the OH stretch and other vibrational modes; (2) large disparity in the mode frequencies.

The resonance energies obtained from the calculations are in reasonably good agreement with the experimental ones, although they are systematically higher. For the (7,0,0) resonance, the computed energies are around 17 cm⁻¹ higher than the experimental one, whereas for (8,0,0), they are about 71 cm⁻¹ higher. These discrepancies—and especially, the trend with increasing energy—are in stark contrast to those of the bound vibrational states not far below the dissociation limit, such as (6,0,0), (4,4,2), (5,2,1), for which the computed energy values are in almost complete agreement with experimental ones^{47,66} (i.e., to within 0.1 cm⁻¹). Of course, the Corrected SPB99 PES was designed to match the bound states only, and so a substantially larger discrepancy is expected for the resonances. Nevertheless, the magnitudes and trend of the errors suggest there may be more to the story.

We offer the following possible explanation: As discussed in Paper I, we discovered a small flaw in the code used to generate the Corrected SPB99 (Ref. 47) values, whereby the actual potential minimum is 5.317 cm⁻¹ lower than what had been presumed previously.⁸⁷ This discrepancy originates from an unexpected small negative contribution of tails of Gaussians used in the correction potential. In any event, given that the perturbative inversion correction still reproduces selected bound states to much higher accuracy than 5 cm⁻¹, this discrepancy may have adversely affected the determination of parameter values obtained in the correc-

TABLE III. Comparison between present calculation and literature values^a for the energies E and widths Γ of the vibrational ($\nu_1, 0, 0$) resonances of HO³⁵Cl.

State label	Literature results		Present calculations	
	E (cm ⁻¹)	Γ (cm ⁻¹)	E (cm ⁻¹)	Γ (cm ⁻¹)
(7,0,0)	21 725.9 ^b	4.98(−4)	21 725.56 ± 0.08	2.68 ± 0.28(−3)
	21 725 ^c	0.01		
	21 709.2 ^d	0.01		
(8,0,0)	24 173.3 ^b	1.9		
	24 172 ^c	0.6		
	24 102.1 ^d	1–3		

^aThe energies are measured with respect to (0,0,0) and $J=0$.

^bFrom Ref. 49.

^cFrom Ref. 50.

^dExperimental results: from Ref. 5.

tion procedure. In particular, in order to accurately reproduce the 22 known vibrational energies up to just below the dissociation limit, the original PES (before correction) might have been artificially distorted upwards in the correction process. Since this process did not make use of the resonance states, we would expect the distortion of the PES to lead to increasingly large overestimates for the computed resonance energies, as the energy increases. Thus, the computed (9,0,0) resonance energy could be too high by hundreds of wave-numbers, although experimental measurements for the (9,0,0) resonance are currently unavailable.

For our previous bound state calculations (Paper I), we showed that near ideality is achieved for the low energy calculations; for the highest bound state energies, even a very large Wyatt block ($W=14\,361$) is only able to reduce the average number of QMR iterations per Lanczos iteration to around $L \approx 30$. This can be attributed to a sudden increase in spectral density near the dissociation threshold, and to the fact that when iterative methods start to “fail” (in the sense of requiring many iterations) performance deteriorates quickly. The (7,0,0) and (8,0,0) states of the present work are at even higher energies and (numerical) density of states. In this and all cases, the “rule” for determining the appropriate Wyatt block size is simply to choose a D for which the total CPU time required is reasonably small. This is not expected to be difficult, as previous experience^{31,32,66} suggests a very slight dependence on D in the vicinity of the optimal value.

For the calculations performed here, we did not expend undue effort trying to locate the optimal D ; we merely tried a few different values before settling on those presented in Table I. It is clear, however, that we are in a large W regime for which the computational bottleneck is the linear algebra manipulations associated with the Wyatt block itself, which implies loss of ideal scaling. For the (7,0,0) calculation, the value $W=17\,549$ was used, which reduces the average number of QMR iterations to just $L \approx 13$. An even larger Wyatt block ($W=20\,341$) was used for (8,0,0), for which the average number of QMR iterations was only $L \approx 23$. Despite the fact that such large W values increase the CPU costs substantially [as per the Eq. (6) formula], the current calculation is still remarkably efficient. Moreover, it is reassuring to observe that W and L are comparable to those of the highest energy bound state calculation from Paper I ($W=14\,361$, $L=29$), despite being around 5000 cm^{-1} above the dissociation threshold.

As for the number of Lanczos iterations, M , we found $M=14$ to be sufficient for both the (7,0,0) and (8,0,0) calculations. This is reasonable for a resonance calculation,³² though a bit larger than what was probably necessary. In any event the ratio of M to the number of desired eigenvalues is larger than in Paper I for three reasons: (1) extraneous non-resonance states are computed; (2) the choice of central energy E was not optimized, but allowed to be off by several wave-numbers; (3) several initial Lanczos iterations are required to “prime the pump,” which has a small but noticeable effect on scaling, particularly for the one-at-a-time calculations performed here. As for (3), we also note that the first few Lanczos iterations tend to require fewer QMR itera-

TABLE IV. Comparison between present calculation and literature values (Weiss *et al.*) for the energies E and widths Γ of the rovibrational (7,0,0) resonances of $J>0$, $K=0$ HO³⁵Cl, for various values of J . All quantities but J are in cm^{-1} .

Angular momentum J	Present calculations		Literature results	
	E	Γ	E	Γ
0	21 725.56	2.68(−3)	21 725.9	4.98(−4)
5	21 740.59	9.47(−4)	21 741.0	1.3(−3)
10	21 780.66	1.79(−3)	21 781.3	1.2(−3)
13	21 816.68	7.54(−3)	21 817.5	3.7(−3)
14	21 830.69	2.46(−2)	21 831.5	3.2(−2)
15	21 845.66	1.63(−2)	21 846.6	2.5(−2)
16	21 861.58	2.65(−2)	21 862.7	1.6(−2)
17	21 878.35	5.81(−2)	21 879.7	3.0(−2)
18	21 897.21	2.75(−2)	21 897.6	8.1(−2)
19	21 916.11	1.64(−2)	21 917.6	8.5(−2)
20	21 936.07	1.22(−2)	21 937.5	3.4(−2)

tions, as the Krylov subspace does not yet overlap much with the numerically problematic eigenstates near E .

B. $J>0$ calculation for (7,0,0) and (8,0,0) resonances

We also performed a series of calculations for the (7,0,0) and (8,0,0) rovibrational resonance states for $J>0$, for various values of $J \leq 20$. In these calculations, the body-fixed angular momentum projection quantum number, K (along the Jacobi vector $\vec{R}$) is chosen to be zero, and Coriolis coupling is ignored. This enables comparisons with the previous calculations, Ref. 49, where a justification for this approximation is also provided. One important difference is that the present calculations utilized the adiabatic rotation approximation^{82,83} for determining the $J>0$ Hamiltonians, rather than the more conventional centrifugal sudden (CS) approximation used in Ref. 49. Qi *et al.*⁸³ showed, in a limited way, that the former approximation should be more general and more accurate. The adiabatic rotation approximation was also used to obtain the $V^J(r, R, \gamma)$ potential function of Sec. III B 2.

Since the $V^J(r, R, \gamma)$ depend on the value of J , one should in principle perform detailed convergence tests for each value of J separately. On the other hand, the J dependence is rather slight, and in addition, $V^J(r, R, \gamma) - V(r, R, \gamma)$ is primarily positive. This suggests that the converged $J=0$ basis should suffice for $J>0$ calculations to comparable energies.⁸⁴ Accordingly, for a given $(\nu_1, 0, 0)$ resonance state, the same basis set was used for all J values (Table I), although some additional convergence testing for $J>0$ was also applied.

Some of our results for different J values are presented in Tables IV and V, for (7,0,0) and (8,0,0), respectively. The corresponding results from Weiss *et al.*⁴⁹ are also presented. The tables indicate that the present calculations are in very good agreement with those of Weiss *et al.* However, a careful inspection reveals that the rotational energy-shifting that emerges from our calculations are a little bit smaller. This discrepancy is almost certainly due to the different approximations that were used for determining the $J>0$

TABLE V. Comparison between present calculation and literature values (Weiss *et al.*) for the energies E and widths Γ of the rovibrational (8,0,0) resonances of $J > 0$, $K = 0$ HO³⁵Cl, for various values of J . All quantities but J are in cm⁻¹.

Angular momentum		Present calculations		Literature results	
J		E	Γ	E	Γ
0		24 174.43	2.39	24 173.3	1.9
2		24 177.37	2.36	24 176.5	2.1
4		24 184.47	2.77	24 183.5	2.6
6		24 195.72	2.58	24 194.6	3.3
8		24 211.04	1.68	24 210.3	3.8
10		24 229.63	1.25	24 230.0	2.7
12		24 252.25	1.54	24 252.6	2.1
14		24 280.15	1.46	24 280.5	1.0
16		24 310.86	6.41(-1)	24 311.2	5.5(-1)
18		24 345.60	1.06(-1)	24 346.2	1.7(-1)
20		24 384.27	3.63(-1)	24 385.2	3.7(-1)

Hamiltonians—i.e., adiabatic rotation versus CS—which give rise to slightly different potentials, $V^J(r, R, \gamma)$.

As further evidence for this claim, we have shown that the averaged rotational constants for our calculations are slightly smaller than the corresponding values from the literature. The rotational constants computed from the present calculations are 0.501 cm⁻¹ for (7,0,0) (determined from the energies for $J=0$ and $J=5$), and 0.491 cm⁻¹ for (8,0,0) (determined from the energies for $J=0$ and $J=2$). Weiss *et al.*⁴⁹ obtained 0.503 cm⁻¹ for (7,0,0), and 0.533 cm⁻¹ for (8,0,0), as computed from their Table II (their reported value for the latter is incorrect). The reported experimental values are 0.496 and 0.495 cm⁻¹, respectively.⁵

The resonance widths Γ as computed for the different J values considered here, are in good agreement with previous experimental and theoretical results. In order to simplify comparisons and highlight J trends, the resonance width data from Tables IV and V is also presented in Fig. 2. One can see that the general tendency and average magnitudes of our results and those obtained by Weiss *et al.*⁴⁹ are quite similar. Nevertheless, Fig. 2 also reveals some small differences between the two calculations over specific J ranges. These suggest that our results are perhaps in better agreement with experimental measurements.

First, most of the data points from our calculations fall well within the upper and lower limits of the experimental values. Callegari *et al.*⁵ reported that the experimental widths for the (7,0,0) resonances, with $J = 13$ –19, lie in the range of 0.015–0.035 cm⁻¹; for (8,0,0) with $J = 0$ –30, the range is 0.5–2.6 cm⁻¹. These limits are indicated by the horizontal lines shown in Fig. 2. Whereas the Weiss *et al.* calculations seem to have a number of significant outliers for both (7,0,0) and (8,0,0), our calculations appear to have only one, for $J = 17$ (7,0,0) (curiously, *not* an outlier for Weiss *et al.*).

Second, the experimental widths for (8,0,0) show a broad maximum at $J = 15$,⁵ in good agreement with the present results (Fig. 2). In contrast, the Weiss *et al.* results are monotonically decreasing over this J range, and exhibit a maximum at the much lower value, $J = 8$. As in the $J = 0$ case, the differences in computed resonance widths, though

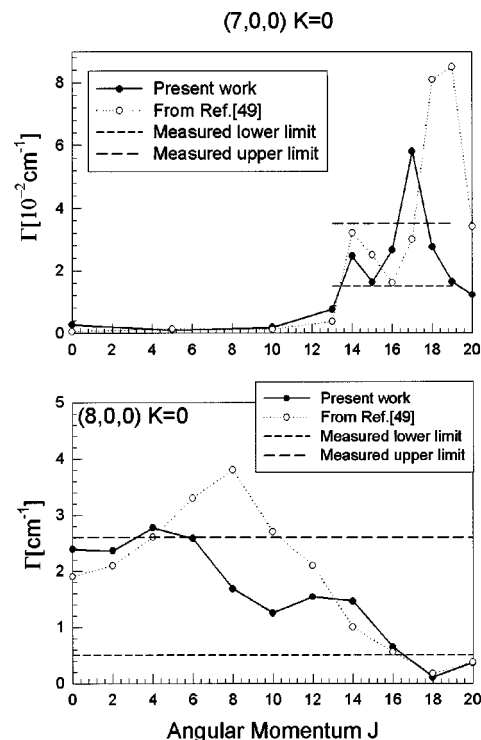


FIG. 2. Comparison between present calculation and literature values (Weiss *et al.*) for the widths Γ of the rovibrational resonances of $J > 0$, $K = 0$ HO³⁵Cl, as a function of J : (a) (7,0,0) resonances; (b) (8,0,0) resonances. Horizontal lines indicate the ranges of experimental measurements (Callegari *et al.*).

small, generally lie outside the convergence error bars of the present calculation.

C. Performance comparison with filter diagonalization

It is of interest to compare the numerical performance of the present PIST/OSBW method, versus that of the FD approach, as used by Weiss *et al.*⁴⁹ When evaluating the performance of different numerical methods, it is almost always difficult to define a fair comparison—owing to different philosophies that may underly the different approaches, idiosyncracies of the particular application under consideration, and the myriad technical issues that inevitably come into play. With regard to a general comparison between PIST/OSBW, a lengthy discussion of these issues is provided in Paper I, in the context of the bound state computation for HOCl, and more generally, in Refs. 31 and 32.

On the other hand, for the particular application considered here—i.e., the calculation of a small number of highly excited mode- and state-specific resonances for HOCl—a numerical comparison is more straightforward than in previous investigations,^{31,32,66} for several reasons. Moreover, we feel that the present application exemplifies the differences in design philosophy between the two approaches. Thus, whereas FD computes a large number of eigenstates for essentially the same CPU effort as would be required for a small number of eigenstates (up to a point), the CPU effort for PIST/OSBW is essentially linear in the number of computed eigenstates. The FD approach provides a great advantage if the spectral window of interest contains a large number of

states. On the other hand, PIST/OSBW will be more efficient in the limit of very narrow spectral windows at very high excitation energies—the most extreme case being that for which just a single eigenstate is computed per calculation.

Thus, whereas in general, the relative improvement in CPU efficiency for PIST/OSBW versus FD depends primarily on the number of states one is interested in, for the present application for which “one-at-a-time” calculations are performed, we expect PIST/OSBW to be favored. Such conclusions are based on theoretical arguments,^{31,32,66} however, necessitating the demand for numerical comparisons to provide more quantitative insight for realistic applications. In this regard, the HOCl resonance application investigated here is ideal.

A second key design philosophy of the present approach follows from the first: since PIST/OSBW is ideally suited to computing small numbers of eigenstates at a time, it is natural to use basis representations that are customized for the states of interest. This has the effect of reducing the total matrix size and (for resonance states) numerical level density, which lowers the CPU cost of the matrix-vector product, as well as reducing the number of linear solver iterations (especially in resonance calculations).³² This idea has been implemented in the present application through the use of the PSO basis representation described in Sec. II A, and especially the modifications described in Sec. III B 1, designed specifically to exploit the mode specificity of the desired resonance states.

Of course, the same sort of basis optimization could be employed in a FD calculation. If many states were desired, as in Paper I, this strategy would require splitting up a single calculation into multiple state- or mode-specific calculations, in order to be effective. Such a multifurcation need not be the most efficient implementation of the FD approach, although it would be ideally suited to a PIST/OSBW calculation. This is why we maintain that the latter approach is more amenable to basis optimization in general, which we in fact regard as being an important part of the method itself. On the other hand, the present resonance application allows us to put all such arguments aside, as the current goal is not to compute *many* states, but rather, a very small, mode-specific few. Accordingly, it is in the best interest of both implementations to use a customized basis set, and indeed, the FD calculations of Weiss *et al.* have also done so. The primary point though is that this leads to more direct comparisons of the two methods.

Another respect in which the comparison is more direct pertains to the PESs used, which for the present application are identical (for purposes of comparison, only $J=0$ is considered). This is in contrast to the bound state calculations of Paper I, for which different PESs were used, leading to complications related to the ranges used for the coordinate r .⁶⁶ For the present comparison, the coordinate ranges appear to be similar, although Weiss *et al.* used $R_{\min}=2.5$ instead of 2.0 [see Eq. (5)]. It should be noted that they report using $r_{\max}=3.5$, which is almost certainly incorrect, because: (1) this is what they used for their earlier bound state calculation using the SPB98 PES, which does not incorporate the HClO isomer;⁶⁶ (2) this would have resulted in a 5 cm^{-1} increase

to the computed energies (Sec. IV A). Most likely, the correct $r_{\max}$ is closer to our value of 6.0.

One somewhat important difference between the two calculations is that ours was performed to a higher level of accuracy—as reflected in the slightly increased coordinate ranges, and the convergence errors as reported in Sec. IV A. This weights the comparison somewhat against PIST/OSBW. On the other hand, our basis set was substantially smaller—despite the increased accuracy—owing primarily to better basis optimization. The latter is more favorable for PIST/OSBW, although we emphasize once again that we regard this as being a part of the method. The increased accuracy is most likely also due in part due to the more efficient CAP used here, although this plays a surprisingly small role in the present case, owing to an atypically small absorbing region (Sec. III B 3).

The issue of basis sets merits further discussion. For our calculation, we used a direct product basis with $(N_R, N_r, N_\gamma)=(150,30,50)$ functions, giving rise to a total basis size of $N=225\,000$. In comparison, the FD calculation used $(220,30,70)$, i.e., $N=462\,000$.⁴⁹ Note that the FD basis is *also* optimized, in that PO DVRs were used for both of the radial coordinates. Curiously, the increase in basis size relative to our basis is actually greater for the optimized N_R than for the unoptimized N_γ . This would not be surprising if slice potentials were used to generate the PO DVRs, as discussed in Sec. II A. Although Ref. 49 does not report how these were generated, we note that the equivalent N_r values suggest that similar effective potentials are being used for $V_r(r)$, which would also be consistent with the slice hypothesis.

Several other, less important issues also come into play, vis-à-vis a numerical comparison of the two approaches. One pertains to the calculation of both eigenvalues and eigenfunctions, versus eigenvalues only. Using FD, the CPU cost of the former is in most cases twice that of the latter, whereas for PIST/OSBW, the costs are essentially the same. On the other hand, FD resonance calculations can gain a factor of two savings in CPU cost, by exploiting a development that converts complex to real arithmetic, which has not yet been applied to PIST/OSBW. All of this serves to emphasize, once again, that a fair CPU cost comparison depends very much on precisely what and how one wishes to compute; for simplicity, we presume in the present application that these two factors of 2 “cancel out.”

Taking the above discussion under consideration, we now present the numerical comparison. Regarding the total number of QMR iterations, we observe a three-order-of-magnitude reduction, from 180 000 for the FD calculation to 184 for the (7,0,0) PIST/OSBW calculation (Table I). This demonstrates the remarkable effectiveness of the OSBW preconditioner, even under very adverse circumstances, and even though ideal scaling is not quite attained. This reduction, moreover, is greater than that observed in any previous numerical comparison with FD,^{31,32} including the bound state HOCl calculation of Paper I. We attribute this to the larger matrices involved here, and also to the fact that PIST/OSBW is favored in the narrow spectral window limit.

On the other hand, the CPU cost per iteration is substantially greater for PIST/OSBW than for FD; and moreover, the

TABLE VI. Comparison of numerical effort required to compute (7,0,0) resonance state for $J=0$ HOCl, using PIST/OSBW vs FD methods. Rows 3 and 4, respectively, reflect PIST/OSBW CPU costs with and without explicit LU decomposition of the Wyatt block. Column II is total number of CPU operations. Column III is the ratio of Column II row 1 to Column II.

Method	Number of CPU operations	Inverse of ratio vs filter diagonalization
Filter diagonalization	2.66 (13)	1.0
PIST w/LU decomposition	1.92 (12)	13.9
PIST w/o LU decomposition	1.15 (11)	232.2

CPU cost of the (one-time) Wyatt block LU decomposition is also very substantial. Accordingly, we also provide a comparison of the total number of CPU operations involved. For PIST/OSBW, this is obtained using Eq. (6); for FD, the formula is $K(N_r + N_R + N_\gamma)N_r N_R N_\gamma$. The results of this numerical comparison, both with and without the Wyatt block LU decomposition, are presented in Table VI. The respective reductions in total CPU effort are around $15\times$ and $230\times$. However, the true savings on our computer platform (Compaq ES45, 1200MHz CPU, 16GB RAM) are in reality *many times greater*, because the memory and compiler architectures are much more efficient for the Wyatt block operations than for the matrix-vector product operations. Similar behavior has been observed on other platforms,³¹ and is anticipated more generally, although to an extent that must be platform-dependent.

In any event, we present data for calculations both with and without the LU decomposition step, because there are several simple techniques that can be used to mitigate the CPU cost of this step—which is now the bottleneck of the entire calculation. For instance, only a single LU decomposition is required for a large number of convergence calculations. Alternatively, one can avoid explicit LU decomposition altogether, by solving the linear algebra problem for the Wyatt block itself at each iteration. This might best be implemented using a “sub-Wyatt,” or even a “recursive Wyatt” approach. As for a recursive implementation of OSB, this is currently being investigated, as is portability to massively parallel computing platforms.

V. SUMMARY

Using an integrative combination of techniques, we have performed an accurate and highly efficient calculation of the (7,0,0) and (8,0,0) resonance states of HOCl, which are states for which the OH bond is selectively and highly excited. This work builds on the previous effort (Paper I) in several important ways: First, resonances well above the dissociation threshold were computed, rather than bound states, requiring the use of the optimized polynomial CAP method (Sec. II B), in addition to the PSO DVR basis, PIST iteration, and OSBW preconditioning methods used previously. Second, the effectiveness of the one-state-at-a-time approach for computing selected mode- and state-specific resonances was evaluated. Third, calculations were performed for the $J>0$ rovibrational resonances, in addition to $J=0$.

Careful convergence studies were conducted, and our calculational results are in very good agreement with those

of Weiss *et al.*,⁴⁹ and Zou *et al.*,⁵⁰ although our results appear to be somewhat more converged. Our calculations reveal that full convergence of states with high overtones of the OH stretching mode requires a large $r_{\max}$. In particular, we find that $r_{\max}=6.0$ bohrs is required, although there is pseudoconvergence in the vicinity of $r_{\max}=3.5\text{--}4.5$ bohrs, which leads to substantially higher computed energies (Sec. IV A). Weiss *et al.*⁴⁹ reported an r range of 1.2–3.5 bohrs for their resonance calculations, which may not be correct, given the very good agreement with the present results.

Good agreement with previous experiments⁵ is also observed (Table II and Fig. 2). By design, the 22 experimentally known vibrational bands are reproduced to very high accuracy by the Corrected SPB99 PES.^{47,66} In contrast, the computed resonance energies for (7,0,0) and (8,0,0) exceed the experimental values by 17 and 71 cm^{-1} , respectively. We believe such large discrepancies may be due to the fact that the actual potential minimum of the Corrected SPB99 PES is -5.317 cm^{-1} , rather than 0 cm^{-1} as presumed by the creators.^{47,87} From this trend, we predict that the computed resonance energy for (9,0,0) would exceed the experimental value by hundreds of wave numbers, although so far, no experimental measurements for this resonance have been conducted.

The present PIST/OSBW calculations used 184 iterations to compute the (7,0,0) vibrational resonance, whereas 180 000 iterations were used in a previous FD calculation⁴⁹ on the same PES. We attribute this remarkable efficiency primarily to the fact that PIST/OSBW is more favored in the limit of narrow spectral windows at high energies, although the basis set and CAP are contributing factors. In any event, it is clear that the present computational scheme is well-suited for computing state-specific and bond-selective features, with “surgical precision.”

On the other hand, the computational bottleneck is now to be found in the Wyatt block manipulations, due to loss of ideal scaling. Consequently, the CPU cost per matrix-vector product is somewhat larger than for the FD calculation, and in addition, a computationally expensive, one-time LU decomposition procedure is required. These additional CPU costs are reflected in Table VI, which underestimates the performance of PIST/OSBW, for reasons explained in Sec. IV C. Techniques for mitigating the cost of LU decomposition will be explored in future papers, wherein we shall also apply the method to more challenging test cases such as acetylene/vinylidene.

ACKNOWLEDGMENTS

This work was largely supported by a grant from The Welch Foundation (Grant No. D-1523). Acknowledgment is also made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the Office of Advanced Scientific Computing Research, Mathematical, Information, and Computational Sciences Division of the U.S. Department of Energy under Contract No. DE-FG03-02ER25534. The authors also wish to express gratitude to Joel Bowman, Tucker Carrington, Jr., Stephen Gray,

Vladimir Mandelshtam, Michael Minkoff, Kirk Peterson, Sergei Skokov, Albert Wagner, and Shengli Zou for many stimulating discussions.

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