Determination of the bound and quasibound states of Ar–HCl van der Waals complex: Discrete variable representation method

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The ArHCl (HCl; ν = 0) van der Waals (vdW) molecule has a large number of bound and rotationally predissociative (resonance) states for total angular momentum in the range of 0 < J < 60. Using the Jacobi coordinates and the total angular momentum representation in the body-fixed reference frame, the Hamiltonian is evaluated in the discrete variable representation (DVR) of the stretch and bend internal vibrational basis and a basis of parity adapted rotation functions. The facile and effective application of the DVR is greatly enhanced by an appropriate choice of the basis set. The sequential diagonalization and truncation of the Hamiltonian permit accurate and efficient determination of eigenstates. Using Hutson’s H6 potential energy surface, the energies and wave functions of all bound and resonance states are computed for selected J’s up to J = 60. A novel flux projection technique facilitates semiquantitative evaluation of the lifetimes of all states and, in particular, the simple identification of the resonance states in the ν2 J2 eigenvector basis.

I. INTRODUCTION

The investigation of the anisotropic intermolecular potentials for the van der Waals (vdW) complex Ar–HCl was initiated by Neilsen and Gordon.1 Using microwave and radio frequency transitions, the molecular beam electric resonance spectroscopy of ArHCl was studied by Klemperer and co-workers.2 Since then enormous efforts have been in progress to achieve a better understanding of the intermolecular interaction between Ar and the diatom HCl. Technologically, the development of the tunable far infrared laser has allowed higher resolution of the spectrum which generally contains much more detailed information about the interaction potential of the vdw complex.3 Theoretically, the intermolecular potential surface of ArHCl has been modified several times to account for new experimental findings.4,6 Subsequent computational studies, involving the then currently available potential surfaces, revealed dynamical properties of the system which gave guidance for further experimental studies. Although a wide variety of computational methods has already been used to solve the Schrödinger equation for systems involving large amplitude motions,6,20 more accurate and efficient numerical approaches are desirable in order to acquire a more complete understanding of the chemical and dynamical properties of the bound and resonance states of polyatomic molecules, including vdw complex.

The computational difficulties in obtaining solutions to the Schrödinger equation for the vibrational motion of vdw complexes is inherent in the shape of intermolecular potential (e.g., for Ar–HCl). The floppiness of Ar–HCl is described by a sharp, repulsive short range interaction and a very slowly varying long range attractive potential between the Ar and the HCl. The intermolecular potential between Ar and HCl is extremely anharmonic, and its effective range of interactions is very broad. The potential energy surface also features a strong coupling of the stretching and the bending motions in the excited vibrational states; this inhibits accurate numerical results via any type of approximation involving separation of the two internal degrees of freedom.14–17

In this paper, a numerical method, based primarily on the discrete variable representation (DVR) that is computationally efficient and remarkably accurate, is proposed and used to solve the Schrödinger equation of the vdw complex Ar–HCl (HCl; ν = 0) to obtain the complete set of bound and resonance states in total angular momentum states up to J = 60. The Hamiltonian is expressed in terms of the Jacobi coordinates, (R, r, θ),13,21,22 and the total angular momentum representation in the body-fixed reference frame. (The coordinate r is fixed at r∗, the equilibrium separation of HCl.) The basis functions for the two internal vibrational motions, namely, the stretching and the bending of the vdw bond are orthogonalized Sturmian functions23 (i.e., associated Laguerre polynomials) and associated Legendre polynomials, respectively. The eigenfunctions of the total angular momentum are used to describe the motion of the body-fixed axis with respect to the space-fixed axis. The Hamiltonian matrix for the internal motion is evaluated in the finite basis representation (FBR) and is orthogonally transformed to the discrete variable representation (DVR).24 (Details of derivations involved in determining the FBR H matrix are given for clarity of numerical procedures; however, in practice, most of terms are evaluated directly in the DVR.) The use of the DVR eliminates the evaluation of all potential matrix elements by integration and requires only the transformation of the (1-D) kinetic energy operators to the DVR. The successive diagonalization and truncation of the lower dimensional DVR Hamiltonian matrices followed by recoupling of the truncated matrices result in significant reduction of the size of the total Hamiltonian matrix. Such efficient reduction is possible due to the sparsity of H in the DVR; this is a general characteristic of DVR Hamiltonians written in orthogonal coordinate systems. Finally, the truncated H matrix is diagonalized to compute accurately the wave functions as well as the energies of eigenstates of the system.
For resonance states, on the other hand, complicated and repetitive numerical techniques are usually required in order to determine their energy levels. Examples of such techniques include evaluating energy derivatives of scattering matrices (i.e., direct scattering solutions of the Schrödinger equation) and the stabilization technique. A numerical method is proposed in this paper which is computationally efficient, and remarkably accurate for the resonance energy levels. These are calculated and identified in a single \( L^2 \) calculation using a semiquantitative flux projection technique for the lifetimes.

In Jacobi coordinates, \( R \) defines the scattering coordinate that denotes the distance between the atom and the center of mass of the diatom. Since the flux is related to motions along the scattering coordinate that is orthogonal to the bending coordinate \( \theta \) the asymptotic flux operator \( \hat{\mathcal{F}} \) is a function of \( R \) only. The flux matrix \( \mathcal{F} \) evaluated for the DVR in the same \( L^2 \) basis (i.e., orthogonalized Sturmian functions) as is used in obtaining the Hamiltonian matrix, is a “one dimensional” imaginary antisymmetric matrix.\(^{22}\) There exist only three distinct eigenvalues for such a “1D” flux matrix, \( \mathcal{F} \); they are zero (degenerate) and two nonzero (a \( \pm \) pair of eigenvalues). The flux matrix \( \mathcal{F} \) can be decomposed into incoming and outgoing flux operators, \( \hat{\mathcal{F}}^+ \) and \( \hat{\mathcal{F}}^- \), that are given in terms of the eigenvectors with positive and negative eigenvalues, respectively.

The outgoing flux operator is constructed naturally\(^{25}\) to be a function of \( R \) only, and thus, greatly simplifies evaluations of its expectation values for eigenstates of a multidimensional \( \mathbf{H} \) matrix. The lifetimes of all eigenstates are estimated semiquantitatively from the computed expectation values of the outgoing flux operator. The resonance width of the \( n \)th excited state, \( \{|n\}\), of the Hamiltonian is simply (approximately) proportional to \( \langle \varphi | \mathcal{F} | \varphi \rangle \), where \( \varphi \) denotes the outgoing flux eigenvector. Relative magnitudes of the computed resonance widths are used to identify clearly (by orders of magnitude) the resonance states from those that are bound or scattering in nature. The computations are performed for a wide range of total angular momentum states (from \( J = 0 \) to \( 60 \)). The estimated lifetimes of resonance states in \( J = 50, 55, 58, 59, \) and \( 60 \) confirm the observed abrupt disappearance of rotational structure in the infrared spectrum above \( J = 60. \(^{26}\)

Hutson’s most updated Model-H6(3) potential energy surface (PES) is used in this work.\(^{14,20}\) The PES was fit analytically to the vdW bond dissociation energy estimated from the observed spectrum.\(^{20}\) The PES describes Ar interacting with nonvibrating rigid rotor HCl. The potential energy surface has two local minima, \( E_{\text{min}} = -174.703, \) and \( -139.533 \) cm\(^{-1}\) at \((R, \theta) = (3.990 \text{ Å}, 0^\circ), \) and \((3.660 \text{ Å}, 180^\circ)\), respectively. The molecular structures for \( \theta = 0^\circ \) and \( \theta = 180^\circ \) correspond to linear configurations of Ar–H–Cl and H–Cl–Ar, respectively. (Refer to Fig. 1.) The surface has the minimum rotational energy barrier of \( E_b = -107.641 \) cm\(^{-1}\) at \((R, \theta) = (3.884 \text{ Å}, 99.0^\circ)\). The lowest energy level among all bound states for ArHCl, therefore, corresponds to localization of Ar around \( \theta = 0^\circ \) with a maximum probability at \( \theta = 0^\circ \).

The following section contains detailed derivations for general theory and numerical procedures proposed and used in this work. The results and discussion are reported in Sec. III with a brief summary in Sec. IV.

II. NUMERICAL METHODS

The general theory and numerical procedures used are described in this section in the following order: (1) The Hamiltonian is written in Jacobi coordinates \( (R, r_s, \theta) \) and total angular momentum representation of the body-fixed reference frame. (2) The finite basis representation (FBR) is formulated using the basis consisting of products of orthogonalized Sturmian functions, associated Legendre polynomials, and parity adapted rotation functions.\(^{13}\) (3) The FBR of the Hamiltonian is defined. (4) This finite basis representation is then transformed to the DVR via an orthogonal matrix transformation. (5) The DVR permits the sequential diagonalization/truncation method to be applied to reduce the \( \mathbf{H} \) matrix. The truncated \( \mathbf{H} \) matrix is finally diagonalized to obtain eigenvalues and eigenvectors. The reduction of \( \mathbf{H} \) does not result in any significant loss of information or accuracy. Finally, (6) the flux projection technique is presented. In order to directly evaluate the outgoing flux for an eigenstate of the Hamiltonian, the flux operator is decomposed into component operators for incoming and outgoing flux.\(^{25}\)

A. Hamiltonian

In the Jacobi coordinate system and the total angular momentum representation of the body-fixed reference frame, the Hamiltonian operator\(^{6,14,21,22}\) of ArHCl (with fixed \( r \) at \( r_s \)) is written as

\[
\hat{H}(R, \theta, \hat{\mathcal{J}}_x, \hat{\mathcal{J}}_y, \hat{\mathcal{J}}_z) = -\frac{\hbar}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu} \left( \frac{1}{R^2} + \frac{1}{r_s^2} \right) \left( -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \right) + \frac{1}{2\mu R^2} \left( \hat{J}_x^2 - 2\hat{J}_y^2 \right) + \frac{\hbar}{2\mu R^2} \frac{\partial}{\partial \theta} \left[ \hat{J}_x (\hat{J}_x + \hat{J}_y) + (\hat{J}_x - \hat{J}_y) \right] + \frac{\hbar}{2\mu R^2} \frac{\partial}{\partial \phi} \left[ \hat{J}_x (\hat{J}_x + \hat{J}_y) - (\hat{J}_x - \hat{J}_y) \right] + V(R, \theta),
\]

where

\[
\begin{align*}
\mu &= \sqrt{m_{Ar} m_H m_{C{l}}} / M, \\
R &= \mathcal{B}/S, \\
r_s &= r_s^* / S,
\end{align*}
\]

for

\[
M = m_{Ar} + m_H + m_{C{l}}, \quad S = \left[ \frac{M m_{C{l}} m_{C{l}}}{m_{Ar} (m_H + m_{C{l}})^2} \right]^{1/4}.
\]
The parameters $\mathcal{R}$, $r_1^*$, and $\theta$ denote a set of Jacobi coordinates; namely, $\mathcal{R}$ is the distance between Ar and the center of mass of HCl, $r_1^*$ is the H–Cl bond distance fixed at the equilibrium value in its ground vibrational state, and $\theta$ is the angle formed by $\mathcal{R}$ and the bond of HCl $R$ and $r_2$ are the mass-scaled Jacobi coordinates that correspond to $\mathcal{R}^*$ and $r_1^*$ with respect to the scaling factor $S$, $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are the operators for $x$, $y$, and $z$ components of the total angular momentum vector, $\mathbf{J}$, in the body-fixed frame. The $\hat{z}$ axis of the body-fixed frame lies along the Jacobi coordinate $\mathcal{R}$. The components of the total angular momentum operator, namely $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ are functions of Euler angles $(\xi, \phi, \eta)$, where $\rho$ denotes the polar angle between the body-fixed $\hat{z}$ axis and the space-fixed $\hat{Z}$ axis.

For simplicity of notation we can define the operators

$$\hat{D}^{\mathcal{R}} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \mathcal{R}^2},$$

$$\hat{D}^{\mathcal{R}^*} = \frac{\hbar^2}{2\mu} \left( -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{J_z^2}{\sin^2 \theta} \right),$$

$$\hat{A} = \hat{J}_x \left[ (\hat{J}_x + \hat{J}_y) + (\hat{J}_x - \hat{J}_y) \right],$$

$$\hat{B} = \hat{H} \left[ (\hat{J}_x + \hat{J}_y) - (\hat{J}_x - \hat{J}_y) \right].$$

The Hamiltonian can now be written as

$$\hat{H}(R, \theta, \hat{J}_x, \hat{J}_y, \hat{J}_z) = \hat{D}^{\mathcal{R}} + \left( \frac{1}{R^2} + \frac{1}{r_1^*} \right) \hat{D}^{\mathcal{R}^*},$$

$$+ \frac{1}{2\mu R} \left[ (\hat{J}_x^2 - 2\hat{J}_y^2) + \cot \theta \hat{A} \right]$$

$$+ \frac{\partial}{\partial \theta} \hat{B} \right] + V(R, \theta). \quad (1')$$

The first two terms are radial and bending kinetic-energy operators; the terms in the bracket correspond to the total angular momentum operators, nonspherical top rotational coupling operators, and a Coriolis coupling term, and, obviously, the last term is the potential energy.

B. Basis functions

The $n$th wave function of a system with total angular momentum $J$ and parity denoted by $p$ will be expanded as a linear combination of products of orthogonalized Sturmian functions (of order $l$ which is fixed) $\{\mathcal{S}^{(i)}(R)\}$, associated Legendre functions $\{\mathcal{P}^l(\theta)\}$, and parity-adopted rotation functions $\{\mathcal{C}^{lp}_{MK}(\xi, \phi, \eta)\}$. The wave function $\Psi$ is, thus, written as

$$\Psi^p_n(R, \theta, \xi, \phi, \eta) = \sum_{i,K} c^{lp}_{iK} \mathcal{S}^{(i)}(R) \mathcal{P}^l(\theta) \mathcal{C}^{lp}_{MK}(\xi, \phi, \eta). \quad (2)$$

Since we can solve for solutions of each total angular momentum and parity separately, we will often omit the $(J, p)$ superscripts.

In the following, $\{\mathcal{S}^{(i)}\}$ and $\{\mathcal{C}^{lp}_{MK}\}$ are discussed in detail. Because the orthogonality and Gaussian quadrature properties of the associated Legendre polynomials are well known and readily available, $\{\mathcal{P}^l\}$ are not mentioned further, except for the definitions in Eqs. (11), (12), and (20b).

1. Overall rotation functions $\{\mathcal{C}^{lp}_{MK}(\xi, \phi, \eta)\}$

In Eq. (2) the rotation functions $\{\mathcal{C}^{lp}_{MK}\}$ are formed by combining the normalized Wigner rotation functions, $\{\mathcal{D}^{lp}_{MK}\}$, to be orthonormal parity eigenfunctions:

$$\int_0^{2\pi} \int_0^{2\pi} \mathcal{C}^{lp}_{MK} \cdot \mathcal{C}^{lp'}_{MK'} \, d\tau = \delta_{JJ'} \delta_{pp'} \delta_{MM'} \delta_{KK'}, \quad (3)$$

where

$$\mathcal{C}^{lp}_{MK} = \mathcal{N}_{K} \left[ \mathcal{D}^{lp}_{MK} + (-1)^K \mathcal{D}^{lp}_{M-K} \right],$$

$$\mathcal{N}_{K} = [2(1 + \delta_{K0})]^{-1/2},$$

and

$$\int_0^{2\pi} \int_0^{2\pi} \mathcal{D}^{lp}_{MK} \cdot \mathcal{D}^{lp}_{MK'} \, d\tau = \delta_{KK'}. \quad (4)$$

in which $d\tau$ denotes the volume element of the Euler angles. (As in the case of the $\{\mathcal{D}^{lp}_{MK}\}$, the $\{\mathcal{C}^{lp}_{MK}\}$ are eigenfunctions of $\hat{J}^2$. However, $\{\mathcal{C}^{lp}_{MK}\}$ are also the normalized eigenfunctions of the parity operator $\hat\rho$. The parity operator, denoted by $\hat\rho$, inverts spatial coordinates, $X \rightarrow -X$, $Y \rightarrow -Y$, and $Z \rightarrow -Z$. This is equivalent to $x \rightarrow -x$, $y \rightarrow -y$, and $z \rightarrow -z$ as well as $\xi \rightarrow \pi - \xi$, $\rho \rightarrow -\rho$, and $\eta \rightarrow -\eta$. $\hat\rho$ has eigenvalues $p = 0$ for even parity $\mathcal{C}^{lp}_{MK}$, and $p = 1$ for odd parity $\mathcal{C}^{lp}_{MK}$'s. Thus, we have

$$\hat\rho \mathcal{C}^{lp}_{MK} = (-1)^p \mathcal{C}^{lp}_{MK}, \quad (4)$$

According to the convention of designating parity levels as $e$ and $f$ which correspond to the even ($J + p$) and the odd ($J + p$), respectively, $K = 0$ is allowed only for $e$ levels.

Other differences in physical properties of the $\{\mathcal{C}^{lp}_{MK}\}$ from those of the $\{\mathcal{D}^{lp}_{MK}\}$ under finite rotations include the facts that they are not eigenfunctions of $\hat{J}_z$, and the $(\hat{J}_x, \hat{J}_y)$ and $(\hat{J}_x - \hat{J}_y)$ are not the raising and lowering operators of $\{\mathcal{C}^{lp}_{MK}\}$. The effects of these operators are

$$\hat{J}_x \mathcal{C}^{lp}_{MK} = K \mathcal{N}_{K} \mathcal{C}^{lp}_{MK} + (-1)^J K \mathcal{D}^{lp}_{M-K},$$

$$\hat{J}_y \mathcal{C}^{lp}_{MK} = K \mathcal{N}_{K} \left[ \mathcal{D}^{lp}_{MK} + (-1)^J K \mathcal{D}^{lp}_{M-K} \right],$$

$$\hat{J}_z \mathcal{C}^{lp}_{MK} = K \mathcal{N}_{K} \left[ \mathcal{D}^{lp}_{MK} + (-1)^J K \mathcal{D}^{lp}_{M-K} \right],$$

where

$$\Lambda_{JK} = \sqrt{(J + 1) - K(K + 1)}.$$  

Nevertheless, the operators $\hat{A}$ and $\hat{B}$ [of Eq. (1')] which are linear combinations of $\hat{J}_x, \hat{J}_y$, and $\hat{J}_z$ acting on $\{\mathcal{C}^{lp}_{MK}\}$'s yield results which are similar to operations of the raising, lowering and $\hat{J}_z$ operators on $\{\mathcal{D}^{lp}_{MK}\}$.

$$\hat{A} \mathcal{C}^{lp}_{MK} = a_{JK} \mathcal{C}^{lp}_{MK + 1} + a_{JK} \mathcal{C}^{lp}_{MK - 1}, \quad (4d)$$

$$\hat{B} \mathcal{C}^{lp}_{MK} = b_{JK} \mathcal{C}^{lp}_{MK + 1} + b_{JK} \mathcal{C}^{lp}_{MK - 1}, \quad (4e)$$

where
\[
\begin{align*}
 b^+_{jk} &= (1 + \delta_{K0})^{1/2} \Lambda^+_{jk}, \\
 b_{jk} &= (1 + \delta_{K-1})^{1/2} \Lambda^{-}_{jk}, \\
a^+_{jk} &= b_{jk} (K + 1), \\
a_{jk} &= b_{jk} (K - 1).
\end{align*}
\]

These properties are useful in evaluating the Hamiltonian matrix elements.

2. "Sturmian" vibrational functions \( \{ \psi_i^{(R)}(R) \} \)

The stretch motions of vdW molecules are highly anharmonic with very weak bond, large amplitude motion states. For these motions a harmonic oscillator basis is very inefficient. Also, functions such as Chebyshev polynomials which give evenly spaced DVR points are equally inefficient. A Sturmian basis, however, is regular at \( R = 0 \) and corresponds to highly anharmonic radial motion. We have found that Sturmian functions, previously used for this type of motion by Yurtsseev et al., provide, in fact, an excellent basis as compared to harmonic or Chebyshev polynomials. The orthogonalized Sturmian functions are equivalent (within a multiplicative factor) to the normalized associated Laguerre polynomials (with the argument being the actual stretching coordinate) multiplied by the square root of its proper weight function. The DVR for the kinetic energy term for Sturmian functions is slightly more difficult to evaluate than for harmonic functions of Chebyshev polynomials.

The nonorthogonal Sturmian functions, \( \{ S_i(R) \} \), are the normalized solutions of the differential equations:
\[
\left[ -\frac{d^2}{dR^2} + \frac{l(l+1)}{R^2} + \frac{1}{4} - \frac{i}{R} \right] S_i(R) = 0.
\]
(These will be used to define the orthogonal basis of Sturmian functions, \( \{ \psi_i^{(R)}(R) \} \).) From the relations of the \( S_i \) to the hydrogenic eigenfunctions, it can be seen that
\[
S_i(R) = N_i^{(R)} e^{2R^2} R^{l+1} \mathcal{L}^{2l+1}_{l-1} (R)
\]
with the associated boundary conditions that \( \{ S_i \} \) approach zero at both the origin and infinity. Also, the parameter

\[
\mathcal{H}_i^{(R)} = \left( \mathcal{H}^K_{fK} \right)_i \mathcal{H}_i^{(R)} = \left( \mathcal{H}_i^{(R)} \right)_i
\]

in which
\[
\begin{align*}
 D_{ij}^{(R)} &= \langle \psi_i^{(R)} | D^{(R)} | \psi_j^{(R)} \rangle \\
 &= \frac{\hbar^2}{2\mu} \left( [i-l(l+1)-2] \langle \psi_i^{(R)} | \frac{1}{R^2} | \psi_j^{(R)} \rangle - \frac{1}{4} \delta_{ij} \\
 &\quad + \left( i - \frac{1}{2} \right) \langle \psi_i^{(R)} | \frac{1}{R} \psi_j^{(R)} \rangle - \frac{1}{4} \delta_{ij} \\
 &\quad - \sqrt{i(i-1) - l(l+1)} \langle \psi_i^{(R)} | \frac{1}{R^2} \psi_{j+1}^{(R)} \rangle \right),
\end{align*}
\]

range is \( i = 1,2,... \) and \( l = 1,2,..., i-1 \). In Eq. (5a), \( N_i^{(R)} \) is an appropriate normalization constant for the proper weight function, \( 1/R \). \( \{ \mathcal{L}^{2l+1}_{l-1} \} \) are the associated Laguerre functions that are orthogonal with respect to the weight function \( e^{-R^2} R^{2l+1} \); namely, for \( (2l+1) > -1 \), the orthogonal property is given by
\[
\int_0^\infty e^{-R^2} R^{2l+1} \mathcal{L}^{2l+1}_{l-1} \mathcal{L}^{2l+1}_{l-1} dR = \delta_{il} \cdot \frac{(i+1)!}{(i-l-1)!}.
\]

Thus, the Sturmian functions \( \{ S_i \} \) are orthogonal with respect to the weight function, \( 1/R \). Furthermore, the orthonormalized Sturmian functions can be defined as
\[
\psi_i^{(R)}(R) = \sqrt{\frac{1}{R}} S_i(R) = \sqrt{\frac{(i-l-1)!}{(i+1)!}} e^{-R^2/2} R^{l+1} \mathcal{L}^{2l+1}_{l-1}(R)
\]
for which we have the orthonormality relations
\[
\int_0^\infty \psi_i^{(R)} \psi_j^{(R)} dR = \delta_{ij}.
\]
(7a)

For a given \( l \), \( \{ \psi_i^{(R)} \} \) form a complete set of orthogonal basis functions, and \( \psi_i^{(R)} \) satisfies the second order differential equation
\[
\psi''_i^{(R)} + g_i \psi'_i^{(R)} + g_0 \psi_i^{(R)} = 0,
\]
where
\[
g_i = l(l+1) + (1/4), \quad g_0 = -l(l+1) + (1/4).
\]
Equation (8) is self-adjoint.

C. Finite basis representation

Using the orthogonality of the basis functions \( \{ \psi_i^{(R)} \} \), \( \{ \mathcal{P}_K \} \), and \( \{ C_m^{(R)} \} \) of the trial wave function of Eq. (2), the FBR of the Hamiltonian matrix of Eq. (1) is obtained;

\[
\begin{align*}
 D_f^{(R)} &= \langle \mathcal{P}_f^{(R)} | D^{(R)} | \mathcal{P}_f^{(R)} \rangle = \frac{\hbar^2}{2\mu} j(j+1) \cdot \delta_{ij}, \\
 g_i^{(R)} &= \langle \mathcal{P}_i^{(R)} V(R,\theta) | \mathcal{P}_i^{(R)} \rangle, \\
 f_i^{(R)} &= \langle \mathcal{P}_i^{(R)} | \frac{1}{R^2 + \frac{1}{R^2}} | \mathcal{P}_i^{(R)} \rangle, \\
 g_0^{(R)} &= \langle \mathcal{P}_0^{(R)} | \frac{1}{R^2} | \mathcal{P}_0^{(R)} \rangle.
\end{align*}
\]

It must be emphasized that in actual numerical computations the Hamiltonian is not obtained in the FBR. As
shown in the following section most of the terms in Eq. (9) are evaluated directly in the DVR. Only \( \{ D_{ij}^{\theta^p} \} \) and \( \{ D_{ij}^{\theta^q} \} \) are evaluated in the FBR, which then need to be transformed to the DVR via the corresponding direct product of 1D orthogonal matrices. We develop this representation below.

**D. Discrete variable representation**

Although the discrete variable representation (DVR) has been very successfully in a number of problems,\(^{24,25,26,31,32}\) we take this opportunity to discuss the representation more fully and precisely. We have defined above a finite basis representation (FBR) of the Hamiltonian in terms of a direct product of basis functions (e.g., orthogonal polynomials) in each coordinate, together with exact integrals of the matrix elements over the coordinates (volume element). We can now make two statements which succinctly define a DVR, given the FBR.

First, the transformation from the FBR to the DVR is orthogonal (or at least unitary), and therefore the representations are formally isomorphic. The basis functions in the DVR are just linear combinations of the basis functions used in the FBR. Second, as a key to the simplicity of the DVR, we make a numerical quadrature approximation to the potential matrix elements in the DVR.\(^{30(a)}\) This numerical approximation, that coordinate functions (including the potential) are diagonal in the DVR, corresponds to a quadrature approximation. This quadrature approximation is normally excellent with Gaussian quadrature accuracy of order \( N \) when \( N \) is the number of basis functions in each dimension. The DVR is the representation in the finite basis in which the coordinate operator is diagonal.

These two aspects of the DVR-FBR relations are easily illustrated: Consider first the exact evaluation of an arbitrary operator \( \hat{A} \) for one dimensional basis in the DVR, \( \{|\alpha\rangle\} \), and FBR, \( \{|i\rangle\} \).

\[
\text{DVR} A_{i\alpha} = \langle \alpha | \hat{A} | \alpha' \rangle = \sum_{i,i'} \sum_{\alpha} \langle \alpha | i \rangle \langle i | \alpha' \rangle = \sum_{\alpha} T_{i\alpha} \langle \alpha | \hat{A} | \alpha' \rangle \sum_{\alpha} \langle \alpha | i \rangle T_{i\alpha'},
\]

in which the matrix \( \mathbf{T} \) defines the transformation between the DVR and FBR and diagonalizes the FBR of the coordinate operator.

In the coordinate representation, the basis functions of the DVR are related to the basis functions \( \{ \phi_i \} \) of the FBR as follows:

\[
\langle x | \alpha \rangle = \sum_{i=1}^{N} \langle x | i \rangle \langle i | \alpha \rangle = \sum_{i=1}^{N} \phi_i(x) T_{i\alpha},
\]

The basis functions of the DVR are special only in that they are eigenfunctions of the appropriate coordinate operator in the finite basis, with eigenvalues equal to the “DVR points”:

\[
X_{i\alpha} = \langle i | x \rangle,
\]

\[
\mathbf{T}^T \mathbf{X} = \mathbf{P},
\]

where \( \mathbf{P} \) is a diagonal matrix, and its elements define the DVR points, \( \{ x_{\alpha} \} \).

In the DVR, functions [e.g., \( V(x) \)] are approximated by their values at the DVR points. This is equivalent to evaluating the matrix elements in the FBR by an \( N \)-point Gaussian quadrature, provided the basis functions are orthogonal polynomials in the coordinate \( x \) times a square root of their weight function. Namely, the basis functions of the FBR must satisfy an orthogonality condition,

\[
\int \phi_i(x) \cdot \phi_j(x) \, dx = \delta_{ij},
\]

in which \( \phi_i(x) = f_i(x) \cdot \sqrt{w(x)} \). Here, \( \{ f_i(x) \} \) are (normalized) orthogonal polynomials in \( x \) and \( w(x) \) is the proper weight function for \( \{ f_i(x) \} \).

As shown by Dickinson and Certain,\(^{30(b)}\) the transformation matrix in Eq. (17b) yields,

\[
T_{i\alpha} = \sqrt{w(x_i)} \cdot \phi_i(x_{\alpha}),
\]

where the \( x_{\alpha} \) (the eigenvalues of the coordinate operator) are the Gaussian quadrature points, and the \( w_{\alpha} \) are the weights at the specified quadrature point for the polynomials used. Furthermore, the assumption that a function is diagonal in the DVR is equivalent to the Gaussian quadrature evaluation of the FBR matrix elements,

\[
\text{FBR} V_{i\alpha} \approx \sum_{\alpha} \omega_{\alpha} \phi_i(x_{\alpha}) V(x_{\alpha}) \phi_j(x_{\alpha}) = \sum_{\alpha} \omega_{\alpha} V(x_{\alpha}) T_{i\alpha} \sum_{\alpha} \omega_{\alpha} \phi_j(x_{\alpha}) = \sum_{\alpha} \omega_{\alpha} V(x_{\alpha}) T_{i\alpha} = \sum_{\alpha} \omega_{\alpha} T_{i\alpha} T_{i\alpha'} \phi_j(x_{\alpha}) = (\mathbf{T}^T \cdot \text{DVR} \cdot \mathbf{V} \cdot \mathbf{T})_{i\alpha}.
\]

For an \( N \)-function basis, these integrals are thus evaluated exactly to order \( 2N - 1 \) in the polynomial power of the product \( \phi_i \cdot V \phi_j \).

After this lengthy preamble, we return to the explicit evaluation of the Hamiltonian in the DVR for our multidimensional problem. The FBR of the Hamiltonian is explicitly written in Eq. (9) is transformed to the DVR via the orthogonal matrix \( \mathbf{T} \);

\[
\text{DVR} \mathbf{H} = \mathbf{T}^T \cdot \text{FBR} \cdot \mathbf{H} \cdot \mathbf{T} = (\mathbf{R}^T \cdot \mathbf{T} \cdot \mathbf{T}^T \cdot \mathbf{K} \cdot \mathbf{T} \cdot \mathbf{T}^T) \cdot (\mathbf{R}^T \cdot \mathbf{K} \cdot \mathbf{T} \cdot \mathbf{T}^T) \cdot (\mathbf{R}^T \cdot \mathbf{T} \cdot \mathbf{T}^T) \cdot (\mathbf{K} \cdot \mathbf{T} \cdot \mathbf{T}^T),
\]

where \( \mathbf{I}_K \) denotes an identity matrix in \( K \), \( \mathbf{R}^T \cdot \mathbf{T} \) and \( \mathbf{K} \cdot \mathbf{T} \) are the 1D orthogonal FBR to DVR transformation matrices in \( R \) and \( \theta \), respectively. We note that for our system only the bases for the internal variables, \( R \) and \( \theta \), are transformed to the DVR. The coordinate matrices are obtained in the DVR by diagonalizing the FBR:

\[
\Delta = \mathbf{R} \cdot \mathbf{R}^T, \quad \Delta = \mathbf{R} \cdot \mathbf{R}^T,
\]

where \( \mathbf{R} \) and \( \mathbf{X} \) are diagonal representations of the coordinate operators \( R \) and \( x = \cos \theta \), and their eigenvalues define the DVR quadrature points in the coordinate spaces \( R \) and \( \theta \). \( \Delta_\theta \) and \( \Delta_\theta \) are the finite basis representation (FBR) of the coordinate operators in \( \{ x_{\alpha} \} \) and \( \{ x_{\alpha} \} \), respectively.

\[\text{(19a)}\]

\[\text{(19b)}\]
Specifically we have, for the Sturmian and associated Legendre polynomial bases,

\[ \kappa \Delta_{t, i} = \int \mathcal{J}^{(i)}(R) \cdot R \cdot \mathcal{J}^{(i)}(R) \, dR \]
\[ = 2i \cdot \delta_{t, i} - \sqrt{(i+1)(i-1)} \cdot \delta_{t, i+1} \]
\[ - \sqrt{(i-1)(i+1)} \cdot \delta_{t, i+1} \]
\[ = \sum_{\alpha=1}^{N} T_{t, \alpha} \cdot R_{\alpha} \cdot R_{t, \alpha} \]

(20a)

\[ \kappa \delta_{j, j} = \int \mathcal{P}(x) \cdot x \cdot \mathcal{P}(x) \, dx \]
\[ = - \frac{(J+K)(J-K)}{(2j+1)(2j-1)} \cdot \delta_{j, j+1} \]

\[ \sum_{J, K} \sum_{i, J} \kappa T_{J, B} \cdot R_{A} \cdot \mathcal{J} \cdot \mathcal{J}^{(i)}(R) \cdot R_{t, \alpha} \]
\[ = \kappa d_{A, \alpha} \cdot \delta_{B, B} \cdot \delta_{K, K} + \frac{\kappa}{\mu} \cdot \frac{1}{(\frac{2\mu}{K} + \frac{1}{2j})} \cdot \delta_{A, \alpha} \cdot \delta_{K, K} \]
\[ + \frac{\kappa}{2\mu K} \cdot \{ [J(J+1) - 2K^2] \cdot \delta_{A, \alpha} \cdot \delta_{B, B} \cdot \delta_{K, K} - (1 + \delta_{K, 0})^{1/2} \Lambda_{J, B} \cdot \delta_{A, \alpha} \cdot \delta_{K, K+1} \}
\[ - (1 + \delta_{K, 0})^{1/2} \Lambda_{J, B} \cdot \delta_{A, \alpha} \cdot \delta_{K, K-1} \} + V_{A, \alpha}^{(a)} \cdot \delta_{K, K}. \]

(22)

where

\[ \kappa d_{A, \alpha} = \sum_{i, J} T_{i, \alpha} \cdot R_{t, \alpha} \]
\[ \kappa d_{B, B} = \sum_{J, J} T_{J, B} \cdot \kappa d_{A, \alpha} \cdot \delta_{K, K} \]
\[ B_{B, B} = \sum_{J} T_{J, B} \cdot \Lambda_{J, B} \cdot \kappa d_{B, B} \]

We now approximate the potential matrix as diagonal in the DVR. That is, in the standard DVR fashion we set

\[ V_{A, \alpha}^{(a)} = V(R_{A} \cdot \delta_{K, K}) \cdot \delta_{A, \alpha} \cdot \delta_{B, B}. \]

As noted above, this approximation is identical to evaluation of the FBR matrix elements by the appropriate \( N \)-point Gaussian quadrature in each dimension and orthogonal transformation to the DVR.

We note that the structure of the Hamiltonian in the DVR is, in general, highly advantageous, in that it is very sparse, i.e., most elements are known to be identically zero. Such sparsity in the DVR is a result of the fact that in the DVR nondiagonal terms are solely due to (kinetic) operators, and differential operators in the equation are normally separable. Furthermore, the Hamiltonian in a direct product basis (or direct product FBR), when transformed to the DVR, contains coupling due to the kinetic energy operators in each coordinate separately. Equation (22), above, demonstrates a typical, very sparse representation of \( H \) in the DVR, with "one dimensional" coupling due to the kinetic energy operators only and no potential energy coupling. This sparsity permits very efficient solution by the successive diagonalization/truncation procedure used before the DVR-DGB treatment of HCN and \( \text{H}_2\text{O}. \) For the full DVR treatment, the method is succinctly described below.

E. Successive diagonalization truncation

The successive diagonalization/truncation method of evaluating eigenvalues and eigenvectors of a large Hamiltonian matrix in the DVR is especially effective because the coupling in \( H \) is "one dimensional." This method involves breaking down the diagonalization of the full DVR\( H \) into a series of diagonalizations of lower dimensional problems. Each diagonalization of the lower dimensional Hamiltonians is followed by a transformation of the successively higher dimensional Hamiltonians of the DVR to a truncated representation in the eigenvectors of the lower dimension. The uniqueness of our diagonalization/truncation procedure in the DVR include the facts that (1) it does not depend on a form of the potential energy function, (2) it permits diagonal terms of all coordinates to be included in diagonalizations at any level for a better eigenvector basis, (3) the sequence of lower dimensional problems can be chosen solely to enhance the computational efficiency, and finally (4) it provides eigenvectors of lower dimensions which are not biased to any specific portion of the potential energy surface.

Depending on the shape of the intermolecular potential
surface, it may be more efficient to diagonalize the 1D Hamiltonians of either the $R$ or $\theta$ coordinate first. In this work, the initial diagonalization is for the 1D Hamiltonians with respect to the coordinate $R$

$$^{1D}H_{ab\alpha \alpha'} = [R_{ab\alpha \alpha'} + V_{ab\alpha \alpha'} \delta_{\beta \beta'} \delta_{\gamma \gamma'}]^{1D}_{a' \alpha' \alpha} \delta_{\beta \beta'} \delta_{\gamma \gamma'}$$

(23)

in which $\{^{1D}h_{\alpha \alpha'}\}$ are the $\alpha\alpha'$th element of the 1D Hamiltonian matrix in the specified $(\beta, K)$-diagonal block of the 3D $H$ matrix. Each pair of $(\beta, K)$ defines the values for the angle $\theta_{K\beta}$, corresponding to the $\beta$th DVR points in the $(\theta^2)$-basis, and $K$ for the projection of $J$ onto the body-fixed axis. Although we could include the diagonal elements of $\{^{Ks}d_{q\alpha}\}$ from Eq. (22) in Eq. (23), we choose not to here. This makes the subsequent truncations somewhat simpler.

For specified $(\beta, K)$, prior to diagonalization $^{1D}h$ may be truncated to limit the span of the $(\{R_{\alpha}\})$ to include only the DVR points which satisfy a potential energy cutoff

$$V(R_{\alpha}, \theta_{K\beta}) < V_{\text{max}}.$$  

In other words, the dynamics of the system at energy greater than $V_{\text{max}}$ is not of current interest.

The truncated $^{1D}$h matrix is then diagonalized to give

$$^{1D}h^{(\beta K)}_{\alpha \alpha'} = \{^{1D}C^{(\beta K)}_{a \alpha'} , ^{1D}E^{(\beta K)} , \{^{1D}C^{(\beta K)}_{\alpha} \}^T$$

(24)

$^{2D}_h^{(\beta K)} = \sum_{\alpha \alpha'} ^{1D}C^{(\beta K)}_{a \alpha' } \cdot [^{1D}h_{a \alpha'} \cdot \delta_{\beta \beta'} + \frac{1}{R_2^2} \frac{1}{R_3^2} \frac{1}{r_c^2} \{ [J(J+1) - 2K^2] \cdot \delta_{\alpha \alpha'} \cdot \delta_{\beta \beta'} \} \cdot \delta_{KK'} \cdot ^{1D}C^{(\beta K)}_{a \alpha'} ]$

$$= \sum_{\alpha \alpha'} ^{1D}C^{(\beta K)}_{a \alpha' } \cdot [^{1D}h_{a \alpha'} \cdot \delta_{\beta \beta'} + \frac{1}{R_2^2} \frac{1}{R_3^2} \frac{1}{r_c^2} \{ [J(J+1) - 2K^2] \cdot \delta_{\alpha \alpha'} \cdot \delta_{\beta \beta'} \} \cdot \delta_{KK'} \cdot ^{1D}C^{(\beta K)}_{a \alpha'} ]$

(27)

where

$$\Pi_{l \alpha}^{(\beta K)} = \sum_{\alpha} ^{1D}C^{(\beta K)}_{a \alpha} \cdot \frac{1}{R_2^2} \cdot ^{1D}C^{(\beta K)}_{a \alpha}$$

for $l = 1, 2, \ldots, P_{\beta K}$, $\alpha' = 1, 2, \ldots, P_{\beta K}$, and $\beta = 1, 2, \ldots, N_{\beta}$. For each value of $K$, a different size of 2D $h$ may be diagonalized;

$$^{2D}h^{(K)} = \{^{2D}C^{(K)}_{a} , 2^{2D}E^{(K)} , \{^{2D}C^{(K)}_{\alpha} \}^T$$

(28)

The 2D-eigenvector matrix $^{2D}C^{(K)}$ is $L_K \times L_K$ where $L_K = \Sigma_{\alpha = 1}^{N_{\alpha}} ^{1D}P_{\beta K}$. It is again truncated by eliminating those eigenvectors corresponding to high energy scattering states. As mentioned earlier, one can either define an absolute number of vectors to be kept or define an energy cutoff such as

$$^{2D}E^{(K)}_{m} < E^{(1D)}_{\text{cut}}$$

to determine which two dimensional solutions, $\{^{2D}C^{(K)}_{m}\}$, are retained. The truncated 2D-eigenvector basis is denoted as $^{2D}C^{(K)}$, and for each $K$ the number of the retained eigenvectors, $2D N_K$, may vary.

The $\tilde{H}$ of Eq. (26) is now transformed to $\tilde{H}$ in the truncated 2D-eigenvector basis representation;

$$\tilde{H}_{m'M'}^{(K)} = \sum_{\beta \gamma} \sum_{l'l} ^{2D}C^{(K)}_{a \alpha} \cdot \tilde{H}_{ll' \alpha \alpha'}^{(K)} \cdot ^{2D}C^{(K)}_{a \alpha'}$$

$$= ^{2D}E^{(K)} \cdot \delta_{mm'} + \sum_{\beta \gamma} \sum_{l'l} ^{2D}C^{(K)}_{a \alpha} \cdot \frac{\hat{\Pi}_{ll'}^{(\beta \gamma)}}{2\mu R_2^2} \left[ - \left( 1 + \delta_{K0} \right) \right]^{1/2} A_{\beta \gamma} B_{\beta \gamma} \cdot \delta_{KK'} + 1$$

$$- \left( 1 + \delta_{K0} \right)^{1/2} A_{\beta \gamma} B_{\beta \gamma} \cdot \delta_{KK'-1} \cdot ^{1D}C^{(\beta \gamma)}_{a \alpha}$$

(29)

where

$$2DE_m^{(K)} \delta m_m = \sum_{\lambda \beta \gamma} 2\bar{C}^{(K)}_{i \lambda \beta \gamma} \cdot 2\bar{H}^{(K)}_{i \lambda \beta \gamma} \cdot 2\bar{C}^{(K)}_{i \gamma \lambda \beta}.$$ 

We can now look at the dimensions of the resulting matrices to be diagonalized. Initially, the basis set in which the DVR Hamiltonian \( H \) of Eq. (22) was obtained was of dimension \( N_{\text{max}} \), \( (N_{\text{max}} = N_R \times N_\theta \times N_\phi ) \); the successive truncations result in \( \tilde{H} \), which is represented in the 2D eigenvector basis and has a size of \( 2D N_k \times N_k \). We note in passing that the sequential form of the transformations indicated in Eq. (29) requires considerably less memory space than the set of direct DVR to 2D eigenvector transformations.

The final diagonalization of the \( \tilde{H} \) matrix, which contains Coriolis terms, yields eigenvectors and eigenvalues of the full 3D Hamiltonian in the \( \mathcal{L}^2 \) basis. To obtain a spatial representation of the wave function, the eigenvectors of \( \tilde{H} \) can be transformed back to the DVR. In the DVR, the coefficients of a specific eigenvector are equal to that wave function evaluated at the quadrature points with a factor of the square root of the weights associated with the point:

$$C_{nk}^{(a \beta K)} = \sqrt{\omega_n \omega_{nk} \beta K} \cdot \Psi_n (R_a, \theta_{nk}, \phi_{nk}).$$

F. Determination of bound, resonance, and scattering states via the outgoing flux operator

The bound character of a state may be determined by the characteristic distribution of the wave function amplitude in the scattering coordinate, or by determining that its energy is lower than the dissociation energy in a given symmetry. On the other hand, a resonance (quasibound) state can be viewed in terms of a lifetime or, equivalently, an amplitude of flux (out or in) across a surface dividing configuration space between reactant and the dissociated product. The outgoing flux can measure motion along the scattering coordinate which determines the rate of dissociation of a molecule. In Jacobi coordinates, \( R \) corresponds to the scattering coordinate which is orthogonal to the other internal coordinates (and Euler angles). Thus, the flux operator for dissociation is a function of \( R \) only, which greatly simplifies the application below. Here we will show how the outgoing flux operator can be defined and easily applied to identify resonance states and estimate their lifetimes.

Using orthogonal coordinates, \( (R, \beta) \), in which \( R \) represents the scattering coordinate, Miller et al.'s symmetrized form of the flux operator is

$$\tilde{F}_R = \frac{i \hbar}{2\mu} \left[ \delta(R-R_0) \cdot \frac{\partial}{\partial R_0} + \frac{\partial}{\partial R} \cdot \delta(R-R_0) \right]$$

for a flux surface located at \( R = R_0 \). In the \( \mathcal{L}^2 \) representation which consists of the direct product basis, the BFR of the flux matrix is given by

$$\tilde{F}^{(K)}_{ij K'} = \langle C^{(a \beta K)}_{MK} , \tilde{F}^{(K)}_{i \lambda \beta \gamma} \rangle \cdot \langle \tilde{F}^{(K')}_{j \lambda \beta \gamma} , C^{(a \beta K')}_{MK'} \rangle$$

$$= \frac{i \hbar}{2\mu} \left[ \lambda^{(i \lambda \beta \gamma)}(R) \cdot \frac{\partial}{\partial R} \cdot \delta(R-R_0) \right]_{R = R_0}$$

$$- \frac{\partial}{\partial R} \cdot \delta(R-R_0) \cdot \delta_{ij} \cdot \delta_{K'K}.$$ 

This is transformed to the DVR via the orthogonal transformation matrix given in Eq. (19). Because the FBR F matrix is diagonal in \( J \) and \( K \), the DVR of F is also quite simple:

$$F^{(a \beta K)}_{ij K'} = \sum_{\alpha \beta \gamma} \mathcal{R}(\alpha \beta \gamma) \cdot \mathcal{T}_{i \beta \gamma} \cdot \mathcal{T}_{j \alpha \beta} \cdot \delta_{K'K}.$$ 

Since \( \mathcal{F} \) is pure imaginary, singular, and Hermitian, the F matrix is antisymmetric giving rise to a set of only three distinct eigenvalues, \( \lambda, -\lambda, 0 \) [identical for each pair \( (\beta, K) \) ]. The simplicity of the F matrix allows an efficient and accurate Lanczos reduction to a \( 3 \times 3 \) matrix. The positive and negative eigenvalues belong to outgoing and incoming flux eigenvectors, \( \langle + \rangle \) and \( \langle - \rangle \), respectively. Thus, \( \mathcal{F} \) may be decomposed into components of outgoing and incoming flux operators, \( \mathcal{F}_+ \) and \( \mathcal{F}_- \); namely,

$$\mathcal{F}_+ (R) = | + \rangle \langle + | - | - \rangle \langle - |$$

$$= \mathcal{F}_+ (R) + \mathcal{F}_- (R).$$

The lifetime \( \tau_n \) of a resonance state depends on the magnitude of the outgoing flux. An expectation value of the outgoing flux, \( f_n^+ \), for the \( n \)th eigenstate of the \( \mathcal{H} \)-matrix in the \( \mathcal{L}^2 \) space is, now, evaluated by

$$f_n^+ = \langle n | \mathcal{F}_+ | n \rangle$$

$$= \langle n | + \rangle \langle + | n \rangle$$

$$= \lambda \sum_{\beta \gamma} \langle C^{(a \beta K)}_{MK} | + \alpha \rangle^2$$

(34)

in which \( | + \rangle \) and \( | n \rangle \) represent the outgoing flux eigenvector and the \( n \)th eigenstate of the Hamiltonian. \( | + \alpha \rangle \) and \( \{ C^{(a \beta K)}_{MK} \} \) are the coefficients of \( | 1 \rangle \) and \( | n \rangle \) in the DVR, and we can use the fact that \( \mathcal{F}_+ \) is an operator on \( R \) (labeled by \( \alpha \) ) only in the evaluation of Eq. (34). \( f_n^+ \) represents the flux of a molecule in the \( n \)th eigenstate of the Hamiltonian crossing the flux measuring surface in the outward direction. It is thus related to the lifetime of the \( n \)th (resonance) state by

$$\tau_n = \frac{2\pi}{f_n^+} = \frac{1}{\Gamma_n},$$

(35)

where \( \Gamma_n \) is the resonance width.

The flux projection technique, proposed first by Park et al., requires an evaluation of the outgoing flux eigenvector, which is one dimensional being a function of \( R \) only. This single eigenvector is used to estimate lifetimes of all eigenstates of the multidimensional Hamiltonian. The outgoing flux operator appears to be the formally correct operator for evaluation of the lifetime of a resonance state (subject to minor renormalization), since it corresponds to the expectation value of the outgoing flux from a \( \mathcal{L}^2 \) normalized resonance state. Several evaluations for known problems using \( \mathcal{L}^2 \) bases, however, have shown that the lifetimes so calculated for a given state by this technique may vary by, at least, a factor of 4 depending on the basis and position of the measuring surface. Thus, we present this technique as interesting and useful, but only semiquantitative. It serves most conveniently, as shown below, to distinguish the resonance states from scattering states (or resonances with lifetimes \( < 10^{-10} \) s).
III. RESULTS AND DISCUSSION

A. Basis sets, procedures and convergence

In general, an FBR-DVR transformation matrix consists of a direct product of 1D transformation matrices. Consequently, a direct product basis set has been the natural choice of a trial wavefunction for the multidimensional DVR. In this work, however, the FBR of the Hamiltonian in \((R, \theta)\) is the only part that is transformed to the DVR. As given in Eq. (19), \(T = A_T \otimes \theta T \otimes I_k\). Therefore, the non-direct product basis of nonseparable internal and space-fixed coordinates does not result in any difficulty in using the DVR since the appropriate DVR in \(\theta\) can and does depend on \(K\). Facile evaluations of the Hamiltonian in various DVRs allow flexibility in selecting appropriate basis functions for specific characteristics of the given system in each degree of freedom. In the case of ArHCl, our choices were based on some of the following considerations.

The associated Legendre polynomials \(\{P^k(\cos \theta)\}\) are used as the basis functions in the bending coordinate \(\theta\), the polar angle between the diatom and the body-fixed \(z\) axis that is fixed along the vdW bond. This treats the singularities of the operator \(D^0_{\theta\theta}\) [Eq. (11)] at \(\theta = 0, \pi\) properly.

Previously, \(^{19,20}\) Legendre polynomials \(P^k(\cos \theta)\) have also been used in calculations for ArHCl. Our calculations have shown that the use of the \(P^k(\cos \theta)\)-basis results in very poor convergence for \(J \neq 0\). For example, for \(J = 0\) calculations, \(N_\theta = 10\) results is converged bound state energy. In order to obtain eigenvalues for the full 2D Hamiltonian of \(K = 1\) converged to \(\pm 0.001\) cm\(^{-1}\), at least \(N_\theta = 25\) is required for \(P^k_\theta\). However, using the \(\{P^k_\theta\}\) with only \(N_\theta = 0\), the energies were converged to better than \(\pm 0.0001\) cm\(^{-1}\) for \(K = 1\) and for higher \(K\) values.

As a basis in the stretching coordinate, the Sturmian functions have been shown to be extremely effective for a floppy system such as the ArHCl vdW complex. \(^{23b}\) As discussed earlier, the size of the DVR basis must be sufficiently large to span the domain of the extremely broad range of the stretching coordinate. In determining the basis sizes, considerations must also be given to the appropriate spacings between the DVR points. The minimum spacing is determined by the maximum local kinetic energy component of the system in each state. The quadrature point of the Sturmian functions are most narrowly spaced near the origin where the kinetic energy and the gradient of the PES are the greatest. The spacing becomes progressively larger with increasing \(R\); the outer region corresponds to a smaller gradient of the PES and smaller kinetic energy. In our computations, the stretching coordinate in ArHCl is scaled by setting the origin at \(R = 3.0\) Å where the potential ranges from \(\sim 500\) to \(3200\) cm\(^{-1}\) depending on angles. The largest quadrature point is set to be at an arbitrary \(R_f\), determined by the desired accuracy of the last bound state.

As a function of the size of the stretching basis \(N_R\) the convergence study of the energy levels is shown in Table I. Since the first 10 energy levels are the same to the accuracy of \(\pm 0.001\) cm\(^{-1}\) for different \(N_R\)'s, for comparisons only the values of the last six bound states are given in Table I. The converged energy levels of all of the bound states for \(J = 0\) are obtained from diagonalization of the 2D Hamiltonian which is composed from \(1^D P_{\text{out}}/N_R = 33/40\) and \(N_\theta = 10\) for the \(R\)-coordinate range of \(R = [3.0, 16.0]\) Å. \(1^D P_{\text{out}}\) denotes the number of 1D eigenfunctions retained to construct the 2D Hamiltonian. The 1D-eigenvector bases for all \((\beta, K)\) are truncated to be the same size (where \(\beta\) refers to the \(\theta\) DVR point). The size of the basis used in \(^{1D}\) \(h, L\), is equal to \(1^D P_{\text{out}} \times N_\theta\). \(N_\theta\) denotes the number of associated Legendre functions in the bending coordinate, and throughout the calculations \(N_\theta = 10\). The DVR basis is defined within the range of a coordinate space \([R_u, R_f]\) which is appropriately varied to obtain converged results for the specified basis size. \(R_u\) and \(R_f\) are the minimum and the maximum DVR values for the stretching basis of the vdW bond.

The first column in Table I contains the results published by Peet and Yang using the same model potential. \(^{19}\) Their energy levels are calculated for \((L = 500)\) in the product basis of 50 distributed Gaussian functions (DGF) in the coordinate \(R\) and 10 Legendre polynomials in \(\theta\). The first 30 DGFs are evenly placed in \(R = [3.0, 7.0]\) Å, and the semiclassical method has been utilized to place appropriately the remaining 20 beyond \(R = 7.0\) Å.

Compared to the size of the DGF basis used for energy levels given in the first column, a smaller DVR basis is required to obtain all the energy eigenvalues with satisfactory accuracies. This is mainly due to appropriate spacings of the DVR points provided by Sturmian functions (or, more pre-

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**Table I.** Convergence of the energy levels for the \(J = 0\) eigenstates with the number and range of the basis functions in the \(R\) coordinate. The size of the basis functions for the bending coordinate is \(N_\theta = 10\) throughout.

<table>
<thead>
<tr>
<th>(R_u, R_f) (Å)</th>
<th>(1^D P_{\text{out}} / N_R)</th>
<th>(E) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>33/40</td>
<td>10.71, 10.71</td>
</tr>
<tr>
<td>11</td>
<td>28/35</td>
<td>10.71, 10.70</td>
</tr>
<tr>
<td>12</td>
<td>23/30</td>
<td>10.70, 10.70</td>
</tr>
<tr>
<td>13</td>
<td>18/25</td>
<td>10.70, 10.70</td>
</tr>
<tr>
<td>14</td>
<td>15</td>
<td>10.70, 10.70</td>
</tr>
<tr>
<td>15</td>
<td>16</td>
<td>10.70, 10.70</td>
</tr>
</tbody>
</table>

---
cisely, the appropriate nature of the Sturmian basis). Since the ArHCl PES is very steeply repulsive at $R < R_e$ and extremely slowly approaching to a dissociation limit, the basis function oscillations must be more densely distributed near the equilibrium and progressively more largely spaced toward the dissociation limit. The Gauss–Sturmian quadrature points satisfy such pattern, as do the lobes of the Sturmian functions, of course.

For higher angular momentum states, the effective potential energy surface reduces the range of the bound states due to the centrifugal energy contribution. Thus, the minimum basis size required for the $J = 0$ calculations sets the maximum number of basis functions necessary for convergences of higher $J$ states.

**B. Energy eigenvalues of bound and resonant states in $(J > 0)$**

We calculated energy levels of the bound and resonance states for selected total angular momentum states $J = 0$ to 60. Separate calculations were carried out for the odd and even parity states of the total angular momentum state selected. The results given in the tables are obtained for the basis size $N_R = 50$ and $N_p = 10$, for each diagonal $K$ block and for the fully coupled Hamiltonian to $K_{\text{max}} = 4$ (or $J$ if $J < 4$).

For a fixed $(\beta, K)$, $1^D h$ [Eq. (24)] is evaluated for $N_R = 50$ and diagonalized to determine eigenvector basis, $1^{D}C_{(\beta, K)}$. The $1^D$ eigenvector matrix is truncated to $1^{D}_{\text{cut}} (\equiv 1^{D}P_{\text{cut}}) = 40$ for every $(\beta, K)$ to obtain $1^{D}C_{(\beta, K)}$. Each diagonal block in $K$ in the full Hamiltonian is denoted as $2^D h$. $2^D h$ is evaluated in the direct product basis of \{1$^D$C_{(\beta, K)}\} and the DVR of \{\mathcal{P}\}, which is $L (\equiv 1^D P_{\text{cut}} \times N_p) = 400$ in size. Diagonalizations of $2^D h$ give the 2D eigenvector matrices, $2^{D}C_{(K)}$, which are truncated by an energy cutoff condition of $2^D E_{m}^{(K)} < 200 \text{ cm}^{-1}$ to a varying size $2^D N_{K}$ for each $K$. We denote this truncated 2D transformation matrix by $2^D C_{(K)}$. Coriolis $(K, K \pm 1)$ coupling terms in the Hamiltonian are evaluated using the truncated 2D eigenvector basis. The full Hamiltonian, in which diagonal $(K, K)$ blocks are diagonal matrices consisting of \{2$^D$E_{m}^{(K)}\}, is finally diagonalized to obtain the energy levels and the wave functions of all the bound and resonance states.

We find that the lowest energy level for a given $K$ increases with $K$. Table II shows comparisons of the (fully converged) energy levels for the lowest states for different $K$'s in $J = 5, 10, 15, 25, 40$. The tabulated values are the eigenvalues calculated from diagonalization of the 2D Hamiltonians of different $K$'s (neglecting Coriolis coupling) which are obtained for $1^D P_{\text{cut}} / N_R = 33/40$, $N_p = 10$, and $R e = \{3.0 \AA, 16.0 \AA\}$. These are almost identical with the corresponding states evaluated in the full diagonalization (including the Coriolis coupling) that are listed in Table III. This indicates two things: (a) In this system the Coriolis coupling is so weak as to be tractable, if desired, by perturbation theory; and (b) our calculations are converged by inclusion of $K$ only to $K_{\text{max}}$. The lowest energy for $K = 5$ is higher than the energy cutoff, $E_{2^D}^{\text{cut}}$ (and the dissociation energy).

The accurate converged energy levels for the bound and resonance states are computed by including the Coriolis $(K, K \pm 1)$ coupling between different $K$ blocks, and diagonalizing the full Hamiltonian. These levels are converged by inclusion of $K$ blocks and coupling from $K = 0$ to $K_{\text{max}}$. As a check, the accurate energy levels of bound and resonance states in $J = 5$ were computed for $K_{\text{max}} = 3, 4,$ and 5. The energy levels calculated for $K_{\text{max}} = 4$ and 5 are identical to 0.0001 up to $E = 150 \text{ cm}^{-1}$ and thus are completely converged with respect to $K_{\text{max}}$. For the case of $K_{\text{max}} = 3$, the energy levels of states up to the last resonance state are also the same to $\pm 0.001 \text{ cm}^{-1}$. (However, the resonance state of $E = 112.145 \text{ cm}^{-1}$ which is obtained from calculations with $K_{\text{max}} = 4$ or 5 is absent for $K_{\text{max}} = 3$.) These calculations show that $K_{\text{max}} = 3$ is sufficient to determine converged energy levels of all the bound and resonance states for each $J$, at least for the ArHCl system under discussion.

Due to the weak $K$ couplings in ArHCl, even smaller calculations may be useful. We find that for all $J E_{2^D}^{\text{cut}} = 20 \text{ cm}^{-1}$ and $K_{\text{max}} = 2$ yield sufficient number of 2D eigenvectors to evaluate the full Hamiltonian. Furthermore, for bound states we then obtained converged eigenvalues of $\mathbf{H}$ for a maximum representation size of $\Sigma K 2^D N_k = 110$. A minimum value of $E_{2^D}^{\text{cut}} = 150 \text{ cm}^{-1}$ and $K_{\text{max}} = 4$ is, however, necessary for converged energy levels of resonance states up to $E = 120 \text{ cm}^{-1}$. However, even this truncates the 2D eigenvector basis to a size of $\Sigma K 2^D N_k < 400$. Note also that we used a much larger number of stretch basis functions $N_p$ than was required for convergence (as shown in Table I). This was necessary in order to extend the $R$-coordinate range for proper evaluation of the flux operator technique for resonance widths, and for identification of resonant states. The lifetimes of resonance states are estimated via the flux projection technique, and the coordinate range must be large enough to avoid spurious edge effects.

A complete listing of energy levels for bound states and resonance states with lifetime longer than 0.1 $\mu$s are given in Table III for $J = 0, 1, 2, 5, 10,$ and 25. The tabulated eigenvalues for bound states are converged to $\pm 0.0001 \text{ cm}^{-1}$. For those resonance states with lifetimes longer than $10^{-8}$ s, the energy levels are accurate to 0.001 cm$^{-1}$. The (Heisenberg) uncertainties in the computed energies of the resonance states with $\tau = 10^{-6}, 10^{-7},$ and $10^{-8}$ s are roughly $\pm 0.001, \pm 0.005,$ and $\pm 0.01 \text{ cm}^{-1}$, respectively.

Perhaps surprisingly, a number of positive energy states for $(J = 1, p = 0)$ and $(J = 2, p = 1)$ are truly bound states of the system. Because of the conservation of parity, $K = 0$ is
### TABLE III. Energy levels of bound and resonance states, for selected J and parity as shown. Resonance states with $r > 0.1 \mu s$ are listed here. For a further detail, refer to the text.

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<tr>
<td>18</td>
<td>-46.223 (bound)</td>
<td>18</td>
<td>-77.593 (bound)</td>
<td>19</td>
<td>-5.313 (bound)</td>
<td>20</td>
<td>-14.077 (bound)</td>
<td>20</td>
</tr>
<tr>
<td>19</td>
<td>-40.280 (bound)</td>
<td>19</td>
<td>-49.335 (bound)</td>
<td>20</td>
<td>-10.829 (bound)</td>
<td>21</td>
<td>-53.621 (bound)</td>
<td>21</td>
</tr>
<tr>
<td>20</td>
<td>-36.713 (bound)</td>
<td>20</td>
<td>-42.508 (bound)</td>
<td>21</td>
<td>-10.829 (bound)</td>
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<td>-46.223 (bound)</td>
<td>22</td>
</tr>
<tr>
<td>22</td>
<td>-29.659 (bound)</td>
<td>22</td>
<td>-25.743 (bound)</td>
<td>23</td>
<td>-10.829 (bound)</td>
<td>24</td>
<td>-32.623 10^{-7}</td>
<td>24</td>
</tr>
</tbody>
</table>

allowed only for those states with even \((J + p)\) values. Calculations for the odd parity states of even \(J\) or even parity state of odd \(J\) do not include \(K = 0\) block of the \(H\) matrix. Since \(\mathbf{J} = \mathbf{l} + \mathbf{j}\) and \(\mathbf{l}\) projects perpendicular to the atom-diatom vector \(\vec{R} = [1 \ 1 \ \vec{R} = \vec{z}]\), where \(\mathbf{l}\) is the orbital angular momentum for the relative motion of Ar with respect to the diatom, \(K\) denotes the projection of \(\mathbf{j}\) (as well as \(\mathbf{J}\)) onto the body fixed \(\vec{z}\) axis (see Fig. 1.) The asymptotic rotational quantum number of HCl, \(j\), is restricted such that \(j > K\) which defines the minimum \(j\) allowed for a given \(K\). Thus, the conservation of parity requires the asymptotic limit of the odd \((J + p)\) states to dissociate to a diatom in its first excited rotational state \((j = 1)\) or higher. Thus depending on the specific parity of the given total angular momentum state, the bound states may have positive energies which are below the energy level of the first excited rotational state of HCl. As shown in Table III A, for example, the \(J = 1(E)\) state supports six bound states that have energies above the \(j = 0\) dissociation limit. \((E)\) denotes the even parity state, for which \(p = 0\). The \(J = 1(E)\) eigenstates with positive energies (less than the \(j = 1\) rotational energy of HCl, \(\sim 20.9\) \(\text{cm}^{-1}\)) are bound because of the conservation of parity.

The probability distribution \(P_n\) of a bound state wavefunction in the bending coordinate \(\theta\) can be expressed in the FBR as

\[
P_n(\theta) = \left[\sum_{K=0}^{K_{\text{max}}} \sum_{j=K}^{N_j} c_{jk}^n \mathcal{P}_j^K(\cos \theta)\right]^2
\]

in which \(\{c_{jk}^n\}\) denote expansion coefficients. For a given \(K\), the lowest bound state is characterized by a localization of \(P_K^{(n)}\) near \(\theta = 0^\circ\). This is due to the dominant contribution from the \(c_{j-KK}^n\) component. Furthermore, the angle at which \(P_K^{(n)}\) is maximum shifts to larger \(\theta\) as \(K\) is increased.

![FIG. 1. Jacobi coordinate system and the total angular momentum representation in the body fixed reference frame.](image-url)
C. Evaluation of lifetimes via the outgoing flux operator projection

The expectation value $f_{n}^{+}$ is related to the rate of dissociation (or lifetime, $\tau_n$) for ArHCl in the n-th eigenstate via Eq. (34). In Table III the estimated lifetimes $\tau_n$ of resonance states are also presented. The states included in the tables are ones that have lifetimes longer than 0.1 $\mu$s, which corresponds to resonance width of 10 MHz. A few states with $\tau_n \sim 0.01 \mu$s are also included in the tables. The tables contain a complete listing of resonance states that may perhaps be observed in an absorption spectrum with high frequency resolution. The laser beam used in the most recent experimental study of ArHCl has a 300 kHz FWHM bandwidth (which corresponds to $\tau_n \sim 1 \mu$s).

Although the lifetime estimates using $f_{n}^{+}$ are not very precise or very accurate, by using them the resonance states are easily distinguished from bound or scattering states without having to evaluate complicated energy derivatives of scattering matrices or stabilizations. Thus this is a very useful approach, easily implemented in this case in the DVR. The outgoing flux operator has an expectation value for all the eigensates of the Hamiltonian in the $l^2$ basis. Their lifetimes, estimated from the outgoing flux, vary by some fifteen orders of magnitude between representations of bound and scattering states. In a typical computation, the total number of eigensates of the Hamiltonian, obtained in the $l^2$ calculation, can be as large as 400. Among the 400 states the majority are obviously discrete approximations to scattering states. Resonance widths of all 400 eigenstates are simply evaluated by projecting onto the outgoing flux eigenvector. According to relative magnitudes of the computed lifetimes of the states, resonance states are clearly distinguished from bound or scattering states of the Hamiltonian in the $l^2$ basis. Thus, we identify resonances with unbound states which have estimated lifetimes longer than $10^{-8}$ s with reasonable confidence.

The outgoing flux eigenvector used to estimate the lifetimes was evaluated for the flux surface placed at $R_1 = 14.9$ Å in the coordinate range of the basis of $R \in [3.0 \text{ Å}, 19.0 \text{ Å}]$. A majority of resonance and scattering states obtained in

| TABLE IV. Energy levels and lifetimes of resonance states in $J = 50, 55, 58, 59, \text{ and } 60$ of positive $(J + \rho)$ states. |
|---|---|---|---|---|
| $(J, \rho)$ | $E(\text{cm}^{-1})$ | $\tau(s)$ | $(J, \rho)$ | $E(\text{cm}^{-1})$ | $\tau(s)$ |
| 50, even | 20.598 | $10^{-3}$ | 55, odd | 47.998 | $10^{-2}$ |
| 42.006 | $10^{-5}$ | 58, even | 65.224 | $10^{-4}$ |
| 48.206 | $10^{-4}$ | 59, odd | 71.112 | $10^{-3}$ |
| 64.42 | $10^{-6}$ | 60, even | 77.05 | $10^{-8}$ |

| TABLE V. Estimated lifetimes $\tau$ of $J = 1$ resonance states, for various $R_n$. The bound and resonance characters of states in the odd and even parities are compared at each energy level. $[R_n, R_f]$ denotes the $R$-coordinate range for the DVR basis, and $R_s$ is the coordinate at which the flux surface is located. |
|---|---|---|---|---|
| $^{1D}P_n/N_n$ | $J = 1(E)$ | $J = 1(O)$ |
| $[R_n, R_f](\text{Å})$ | $[3.0, 16.0]$ | $[3.0, 19.0]$ | $[3.0, 25.0]$ | $[3.0, 16.0]$ | $[3.0, 19.0]$ | $[3.0, 25.0]$ |
| $R_s (\text{Å})$ | 12.2 | 14.9 | 20.3 | 12.2 | 14.9 | 20.5 |
| $E(\text{cm}^{-1})$ | $-83.771$ | $10^{-3}$ | $10^{+3}$ | $-117.709$ | $-94.050$ | $10^{-2}$ |
| $-55.165$ | $10^{-1}$ | $10^{-2}$ | $10^{+5}$ | $-85.290$ | $-83.768$ | $10^{-1}$ |
| $-48.552$ | $10^{-1}$ | $10^{-3}$ | $10^{+4}$ | $-66.900$ | $-59.647$ | $10^{-1}$ |
| $-31.064$ | $10^{-1}$ | $10^{+1}$ | $10^{+2}$ | $-55.163$ | $-48.990$ | $10^{-1}$ |
| $-20.340$ | $10^{-1}$ | $10^{+1}$ | $10^{+2}$ | $-48.422$ | $-41.753$ | $10^{-1}$ |
| $-12.192$ | $10^{-1}$ | $10^{+1}$ | $10^{+1}$ | $-31.062$ | $-25.818$ | $10^{-1}$ |
| $0.776$ | $10^{-1}$ | $10^{+1}$ | $10^{+1}$ | $-22.771$ | $-20.342$ | $10^{-1}$ |
| $3.653$ | $10^{-2}$ | $10^{+1}$ | $10^{+1}$ | $-16.970$ | $-12.195$ | $10^{-1}$ |
| $10.701$ | $10^{-1}$ | $10^{+1}$ | $10^{+1}$ | $-12.195$ | $-11.735$ | $10^{-1}$ |
| $14.659$ | $10^{-2}$ | $10^{+3}$ | $10^{+1}$ | $-7.793$ | $-5.416$ | $10^{-2}$ |
| $16.603$ | $10^{-2}$ | $10^{+1}$ | $10^{+1}$ | $-1.852$ | $-0.337$ | $10^{-2}$ |
| $19.550$ | $10^{-4}$ | $10^{+1}$ | $10^{+1}$ | $0.777$ | $3.663$ | $10^{-2}$ |
| $20.704$ | $10^{-10}$ | $10^{+2}$ | $10^{+2}$ | $10.703$ | $14.51$ | $10^{-2}$ |
| & | $10^{-9}$ | $10^{-9}$ | $10^{-9}$ | $10.703$ | $16.603$ | $10^{-2}$ |
| & | $10^{-8}$ | $10^{-8}$ | $10^{-8}$ | $19.545$ | $16.603$ | $10^{-2}$ |
| & | $10^{-7}$ | $10^{-7}$ | $10^{-7}$ | $20.697$ | $16.603$ | $10^{-2}$ |
computations have $\tau_\alpha < 0.1 \mu s$ ($\sim 10$ MHz), which are not reported in the tables. The energy levels given in Table III are for bound states and resonance states that have sufficiently long lifetimes ($> 0.1 \mu s$). In Table IV, the energy levels of the lowest energy states and their estimated lifetimes are presented for resonance states in $J = 50, 55, 58, 59,$ and $60$. The lifetimes clearly indicate an absence of resonance states with $\tau_\alpha > 0.01 \mu s$ beyond $J = 60$. This confirms the observed infrared spectrum of ArHCl which showed an abrupt disappearance of rotational structures for $J > 60$.

Table V gives the variation of estimated lifetimes of the $J = 1$ eigenstates of both even and odd parities which yield $\tau_\alpha > 10^{-7}$ or $10^{-8}$ for the largest basis. The $\tau_\alpha$ values are compared as the position of flux measuring surface is moved out toward the asymptotic limit. (The “lifetime” of a bound state merely refers to a numerical value computed from the expectation value of the outgoing flux operator computed in the $P^2$ basis. The calculated resonance width is non-zero for bound states due to the tail of the wave function at the flux measuring surface.) Because the outgoing eigenvector of the flux operator is calculated at finite $R$ in the $P^2$ basis, its overlap with a bound state wave function will exponentially decrease with an increase of the coordinate value at which the flux measuring surface is placed. Consequently, the lifetimes of bound states will show consistent increases for larger $R$-coordinate ranges. The effect of an increase in the coordinate range will be less significant on the lifetimes of resonant states and be of little significance to scattering states. (The absolute magnitude of the flux projection for bound states may change a lot, but it should remain small.)

In Table V, it may be noted that the estimated lifetime of the last bound state ($E = -0.337$ cm$^{-1}$) in $J = 1(0)$ is much smaller than the lifetimes of other bound states. This is because the classical turning point for the vibration of this state is near the location of the flux surface. The first six of the positive energy levels in $J = 1(E)$ states also show bound characteristics. These states are bound due to the conservation of parity. One also knows, of course, that states with energies below the lowest parity-allowed asymptotic state are bound, so the use of the flux projection techniques on the bound states is really a test of these techniques.

Our “positive flux projection” technique is not quantitative, since the expectation value of the projection, i.e., the lifetime, varies substantially depending on the position of the flux measuring surface. Thus, our estimated lifetimes of resonant states have uncertainties of as much as a factor of 4.
(which occur when the positions of the flux measuring surface are moved). Nevertheless, the relative differences in lifetimes of the bound, resonant, and scattering states are at least 4 or 5 orders of magnitude. Thus, the flux projection technique is a simple means of distinguishing resonance states from either bound or scattering states. The energy levels of resonance states are obtained accurately and simply in the $\mathcal{E}^2$ basis.

D. Types of resonances

It is known that the resonance states in ArHCl can be classified into two types; those that tunnel through the centrifugal barrier and those that rotationally predissociate. Because the rotational constant of the vdW complex is relatively small in comparison to the strength of intermolecular interactions, the centrifugal barrier becomes large enough to support quasibound states only for high $J$ states. The first resonant state ($E = 0.163$ cm$^{-1}$) in $J = 10(E)$ and the first two resonant states ($E = 0.665$, 1.409 cm$^{-1}$) in $J = 25(O)$ are quasibound due to the centrifugal barrier.

The majority of resonant states are rotationally predissociative. The states can be characterized as the bound states of the van der Waals molecule in which the constituting diatom is rotationally excited. Dissociation occurs when excess rotational energy of the diatom flows into the stretching motion of the vdW bond due to the anisotropic intermolecular interaction between the diatom and the atom. Because of the extensive anisotropy, the bending motion (i.e., hindered rotation of the diatom) and the stretching motion of the vdW molecule are strongly coupled.

E. Wave functions

Consistent with the suggestion by Tennyson, the nodal structures of bound or resonant states of ArHCl seem quite irregular for highly vibrationally excited states. For low energy states, the wave functions indicate very weak couplings between different $K$ values. Figure 2 contains the contour plots of selected bound states of $J = 10(E)$. The contours indicate where the wave function has 0.5%, 1.5%, 4%, 8%, 16%, 32%, and 64% of its maximum probability amplitude. The probability amplitudes $P$ of wave functions are computed by integrating over the Eulers angles:

$$P(R,\theta) = \frac{2J+1}{8\pi^2} \int |\Psi|^2 \sin \rho \, d\rho \, d\eta.$$

Among the plots presented in Fig. 2, the first five states show quite regular nodal patterns. The last plot corresponding to the wave function for $E = -14.874$ cm$^{-1}$ starts to show some irregularity.

$(s,b)$ are used to denote the excitations in stretching and bending internal motions; these, however, are not good quantum numbers of the system, although $b$ asymptotically corresponds to the rotational quantum number $J$ for the isolated diatom. $K$, as mentioned earlier, denotes an angular momentum along the internuclear axis $R$. In other words, $K = 0, 1, 2, ... , b$. For highly excited states, because of the strong coupling between the stretching and the bending motions, the assignments of $(s,b)$, however, do not provide accurate descriptions of wave functions. As shown in Fig. 2, the equilibrium linear configuration of Ar–H–Cl shifts to a T shape in the excited states.

Earlier we discussed how the conservation of parity leads to bound states which have energy levels above dissociation limit of HCl($J = 0$) but below the energy of a $j = 1$ state of HCl. Figure 3 contains probability plots of a resonance state with $E = 18.096$ cm$^{-1}$ in the even parity and a bound states with $E = 18.090$ cm$^{-1}$ in the odd parity manifold. The contours are probability amplitudes for 0.01%, 0.05%, 0.2%, 0.8%, 3.0%, 9.0%, 20%, 40%, 80% of its maximum value. The bound character of the state with the odd parity can be compared with that from the resonance state at essentially the same energy.

IV. CONCLUSIONS

In this paper we have examined dynamical characteristics of the ArHCl vdW complex. The interaction potential energies are evaluated using Hutson’s H6(3)-PES. We have demonstrated that the appropriate choice of the basis set can enhance the accuracy and the efficiency of computations in the $\mathcal{E}^2$ basis. Since the DVR is easily set up for any basis and the Hamiltonian evaluation in the DVR is very simple, we are free to choose the most appropriate basis for a given molecule or degree of freedom. In this case, the "Sturmian" basis was well suited to the high anharmonic motion. A direct product basis and DVR is used for internal degrees of
freedom. (The method can fairly easily be extended to include the vibrational motion of the H–Cl stretch.) The sequential diagonalization/truncation yields an optimized basis for each subsequent representation.

The "positive flux" projection technique has been applied to identify resonance states. Expectation values of a one-dimensional outgoing flux operator are evaluated for all eigenstates of the Hamiltonian in the \( \mathcal{L}^2 \) basis. Among \( \sim 500 \) eigenstates which are primarily scattering states, only a few states are identified as resonance states with \( \tau_n \gg 0.1 \mu s \). The method is novel, effective, and very simple, since it involves a single 1D outgoing flux eigenvector in estimating lifetimes of eigenstates of the multidimensional Hamiltonian.

One last note is a comment regarding the recent calculation by Clary et al. for the ArHCl system with slightly different PES than what is used in this work.20 As a check, using the computational method presented in Ref. 20, they carried out a calculation with our PES (namely, Hutson's H6) for \( J = 5 \) (O) and obtained the bound state eigenvalues to within \( \pm 0.02 \) cm\(^{-1}\) of our result shown in Table III.25

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