Differentiation of the ground vibrational and global minimum structures in the Ar:HBr intermolecular complex

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A fully three-dimensional morphed potential energy surface is reported for Ar:HBr. The morphed potential was obtained from parametrized scaling and shifting transformations of an \textit{ab initio} potential. The optimum parameters of the morphed potential were determined by a regularized nonlinear least-squares fit to available experimental data. The rovibrational dynamics of the complex were computed using an adiabatic separation of the H–Br intramolecular stretching mode from the intermolecular modes of the system. The ground rovibrational state of the morphed potential was found to have the hydrogen-bound structure Ar–HBr. This state was 10.99 \text{ cm}^{-1} more stable than the corresponding state having the van der Waals structure, Ar–BrH, in agreement with experimental data. However, the global minimum of the morphed potential was found to have the van der Waals structure, Ar–BrH. This structure was 20.9 \text{ cm}^{-1} lower in energy than the local minimum having the hydrogen-bound structure, Ar–HBr. © 2001 American Institute of Physics. [DOI: 10.1063/1.1379337]

I. INTRODUCTION

Molecules of the form Rg:HX have been the focus of many experimental and theoretical studies.\textsuperscript{1,2} These studies have lead to an understanding of the basic intermolecular forces that are important in a wide variety of systems from condensed phases to protein folding. Recently, a number of studies have considered the potential energy surfaces of the complexes of this series, there are two local minima in the interaction PES. One minimum in the PES occurs when the H atom is between the Ar and X. This minimum is known as the hydrogen bond (HB) isomer and will be denoted Rg–HX. The other minimum in the PES has the H atom pointed away from the Ar atom and is known as the van der Waals (vdW) isomer and will be denoted Rg–XH. The difference between the ground state energies in these two forms, \( \Delta E_0 = E_{0,vdW} - E_{0,HB} \), decreases down the series. The measured or estimated values are 52.0565 \text{ cm}^{-1} in Ar:HF, 23.6572 \text{ cm}^{-1} in Ar:HCl, 10.99487(13) \text{ cm}^{-1} in Ar:H\text{Br}, and \(-7.89 \text{ cm}^{-1}\) in Ar:HI. Note that as one proceeds down the periodic table the vdW form becomes more stable with respect to the HB form so that at Ar:HI, the vdW form is the most stable form, with the HB form not yet having been experimentally observed. A comparison between theory and experiment of these energy differences requires two steps. First the underlying three-dimensional PES must be evaluated, then the vibrational states must be computed. Thus the energy differences given above have two components, the underlying differences in the interaction potentials and the differences of the zero-point energies of the two structures.

One approach to make the connection between the experimental observations and the underlying interaction energy is to assume a functional form for the interaction potential with a number of adjustable parameters. The adjustable parameters are then optimized until a best fit with the experimental data is obtained. An uncertainty associated with this derived potential can be obtained by computing the range of parameters that yield a quality of fit that is within a certain range of values of the optimal fit.\textsuperscript{18} However this type of error estimate is still constrained by the functional form originally assumed. One method of this type, which seems to be particularly promising, is the PES morphing approach.\textsuperscript{14,15,19,20} Earlier work\textsuperscript{19,20} used a functional form where the potential was decomposed into a sum of attractive and repulsive terms that were then computed separately using \textit{ab initio} methods. Latter work\textsuperscript{14,15} used an assumed functional form that was a complete \textit{ab initio} PES. In these studies, the complete \textit{ab initio} PES was then fit to an analytical form. A set of adjustable parameters were chosen to describe various scaling and shifting transformations, i.e., morphing transformations, on the \textit{ab initio} PES. The \textit{ab initio} PES was then morphed to obtain optimal agreement with observed experimental data. The resulting PES represents a combination of experimental information in the regions of the potential that can be determined from the experimental data and \textit{ab initio} information to determine regions of the PES for which there is no experimental data. The method of complete \textit{ab initio} PES morphing has been previously applied to the intermolecular degrees of freedom for atom–diatom molecular dimers.\textsuperscript{14,15} In this study we extend this approach also to include the intramolecular mode in an atom–diatom system. This extension has also been made previously for the decomposed \textit{ab initio} PES morphing method.\textsuperscript{20}

The direct approach for treating both the intermolecular and intramolecular rovibrational dynamics in an atom–diatom system, such as Ar–HBr considered here, is to expand the wave function in the asymptotic vibrational states.
of the diatomic.21,22 This approach converges rapidly with respect to the number of diatomic vibrational states used since the intermolecular motion only weakly perturbs the intramolecular mode. This weak perturbation is due to the large disparity in characteristic frequencies for the intramolecular and intermolecular motion. One difficulty with this approach when studying the system in excited intramolecular vibrational states is that these states are imbedded in the dissociative continuum. An alternative approach that takes advantage of the disparate characteristic frequencies and circumvents the difficulty of the predissociative intramolecular vibrational excited states is to use an adiabatic separation of the intramolecular and intermolecular modes. Thus for each vibrational state of the intramolecular mode an adiabatic interaction potential is defined, and any nonadiabatic couplings are neglected.

One approach, which has been used to express the dependence of the various adiabatic potentials on the isotopic composition and vibrational state of the diatom,7,8 is to use the mass-reduced vibrational quantum number.23 In this approach one uses the fact that the moments of the PES times the intramolecular vibrational state are simple functions of the mass reduced vibrational quantum number. Thus the adiabatic PES can be expressed as a power series in the mass reduced vibrational quantum number. A PES can then be fit by varying the expansion coefficients. In the present study our interest is in understanding the features of the underlying three-dimensional PES so that we have not used this approach based on the moments of the PES but we have explicitly considered the full three-dimensional potential within the adiabatic approximation.

Previously, the Ar:HBr PES has been studied in its ground and vibrationally excited states.4,12 In these studies the interaction potentials were independently obtained using the differing available experimental data4,12,16,24,25 for the two states of Ar:HBr. These studies lead to qualitatively different potential energy surfaces for the \( \nu_1 = 0 \) and \( \nu_1 = 1 \) interaction potentials where \( \nu_1 \) is the quantum number describing the state of the intramolecular H–Br stretching vibration. The striking difference between these potentials was that in the \( \nu_1 = 0 \) state both the ground state and the global minimum in the adiabatic potential had the HB structure,3 whereas in the \( \nu_1 = 1 \) adiabatic PES the ground state had the HB structure and the global minimum in the potential had the vdW structure.12 In the present study we construct a morphed three-dimensional \textit{ab initio} PES that has been fit to all available experimental data for the \( \nu_1 = 0 \) Ar:HBr, \( \nu_1 = 0 \) Ar:DBr, and \( \nu_1 = 1 \) Ar:HBr adiabatic surfaces. This morphed potential is found to have a ground state with the HB structure and a global minimum with the vdW structure in agreement with the previously obtained \( \nu_1 = 1 \) adiabatic PES. These results suggest that the Ar:HBr system is unusual in having different structures for its ground state and PES minimum. These results also illustrate the fact that potentials based on assumed functional forms and fit to limited data, as was the case in original \( \nu_1 = 0 \) PES study, can lead to qualitatively incorrect interaction potentials.

An example of a previously investigated interaction in which it is possible to differentiate between the ground vibrational structure and the global minimum of the PES is the complex He:Cl\(_2\).26 In that instance the ground vibrational state was found to be T-shaped while the global minimum in the PES was found to be linear. By contrast, the related He:FCl complex27 was found to be linear in both its ground vibrational state and in the global minimum of the PES. These two examples illustrate intricacies of the zero-point energy effects in systems with low energy isomeric configurations. The intermolecular forces in the Ar:HBr complex considered here are different from the He:Cl\(_2\) example, since the Ar:HBr system has stronger hydrogen bond type interactions.

In addition to the specific study mentioned above, we also present here two innovations in the procedures used to study these systems. First we use a modified fitting procedure. The new fitting procedure uses smoothed versions of the kernels of the reproducing kernel Hilbert space (RKHS), it also uses preorthogonalized one-dimensional RKHS kernels, and the logarithm of a shifted and scaled PES is fit rather than the original potential. The smoothed RKHS kernels allow for rapid convergence of the numerical integrals performed. The preorthogonalized RKHS kernels minimized the loss of precision inherent in the use of the nearly linear dependent RKHS kernels. The use of the logarithm of the potential leads to a better extrapolation to the repulsive regions of the PES. The second change in our morphing method is to use a regularized least-squares fit to the experimental data. This greatly speeds up the convergence to the best fit by reducing the linear dependence of the parameters used to morph the potential. Additionally, the regularization parameter also allows one to define a sequence of morphed potential that smoothly connects the \textit{ab initio} PES to the best-fit morphed PES.

II. METHODS

A. \textit{Ab initio} calculations

The nonrelativistic interaction energies of the Ar:HBr complex were calculated using second-order Möller–Plesset perturbation theory (MP2) with a 6-311++G(3pd, 3df) basis set using the \textsc{gaussian} electronic structure package.28 A grid of 560 \((R, \theta, r)\) points were calculated as follows: The HBr bond distance, \(r\), was varied using the eight point grid 1.2143 Å, 1.2643 Å, 1.3143 Å, 1.4143 Å, 1.5500 Å, 1.6000 Å, 1.6500 Å, 1.7000 Å, while 10 equally spaced points between 3.1932 and 5.4432 Å along the \(\text{H–Br–Ar}\) angle, \(\theta\), were calculated. To account for basis set superposition error (BSSE), the calculated interaction energies were corrected at every grid point using the Boys and Bernardi counterpoise correction.29 The interaction energies were thus calculated as the energy difference between the energy of Ar:HBr complex and the energies of the Ar atom and of the HBr diatom at every calculated point using the 6-311++G(3pd, 3df) basis sets on all atomic centers of the dimer. Finally, a full BSSE corrected three-dimensional PES was obtained by using

\[
V(R, \theta, r) = V^\text{mm}(R, \theta, r) + V^{\text{HBr}}(r),
\]
where \( V^{\text{int}}(R, \theta, r) \) is the BSSE corrected interaction energy and \( V^{\text{HBr}}(r) \) is the interatomic potential for the isolated HBr molecule. In this study we have taken \( V^{\text{HBr}}(r) \) to be a one-dimensional Morse potential \((2)\) with the parameters \( \beta = 2.311 \text{ cm}^{-1} \), \( D = 38.796.63 \text{ cm}^{-1} \), and \( r_c = 1.41436. \text{ Å} \). All calculations presented in this study are for complexes and monomers containing the \(^7\)Br isotope. With the Morse potential given here, the fundamental transition energy for \(^7\)Br monomer is the same as the experimental value of 2558.9 cm\(^{-1}\).31

**B. Interpolation of the PES**

As indicated above, the PES of Ar:HBr is a function of three coordinates, \( R, \theta, \) and \( r \). Given the \textit{ab initio} PES computed on a three-dimensional grid of points we then need to interpolate the \textit{ab initio} points to an arbitrary grid of points. To carry out this interpolation, we have used a modified form of the RKHS interpolation method which has been discussed by Rabitz and co-workers.14,32,33 and which we have used previously to study molecular complexes.14 In this study, we used a direct-product grid, i.e., given sets of \( R, \theta, \) and \( r \), points, the three-dimensional grid was formed by taking all possible combinations of the \( R, \theta, \) and \( r \), points. The corresponding RKHS fitting functions also were formed as a direct product of sets of the one-dimensional RKHS kernels for each coordinate.

In the \( R \) direction we used a smoothed distancelike RKHS fitting function of the form

\[
q_1(R, R', \Delta R) = \frac{1}{14R^7} \left[ 1 - \frac{7R'}{9R} \right] W(R, R', \Delta R) + \frac{1}{14R^7} \left[ 1 - \frac{7R}{9R} \right] \times \left[ 1 - W(R, R', \Delta R) \right],
\]

where \( W \) is a switching function defined as

\[
W(x, x', \Delta x) = \frac{\exp(\alpha(x, x', \Delta x))}{\exp(-\alpha(x, x', \Delta x)) + \exp(\alpha(x, x', \Delta x))}
\]

and

\[
\alpha(x, x', \Delta x) = \frac{x - x'}{\Delta x} + \frac{(x - x')^3}{\Delta x},
\]

where we have taken \( \alpha = (1/2) \tanh^{-1}(0.8) \) and where \( \Delta x \) defines the range of the switching. This fitting function, \( q_1 \), is a smoothed version of \( q^{\text{int}}_{1,m=6} \) as defined by Ho and Rabitz.32 As noted by Ho and Rabitz, \( 1 \) reproducing the reproducing kernels \( q^{\text{int}}_{1,m=6} \) will yield the correct functional form of the potential (1/R\(^6\)) if a continuous set of reproducing kernels is used. When a quadrature approximation is used, i.e., a finite set of reproducing kernels as used in this study, the reproducing kernels will only give the correct functional form for the values of \( R \) less than the location of the last reproducing kernel. One would then expect at some larger \( R \) a noticeable difference between the correct and extrapolated functional forms. Thus the morphed potential developed here will be most appropriate for \( R < 5.5 \text{ Å} \) and will have small errors when extrapolated to larger values of \( R \).

We used an angle like RKHS kernel for the \( \theta \) direction that is given by

\[
q_2(y, y', \Delta y) = 1 + yy' + 2yy'^2 \left[ 1 - \frac{y'}{3y} \right] W(y, y', \Delta y) + 2y'^2 \left[ 1 - \frac{y}{3y'} \right] [1 - W(y, y', \Delta y)],
\]

where \( W \) is the same switching function as defined in Eq. (3) and \( y(\theta) = (1 - \cos \theta)/2 \). The fitting function \( q_2 \) is a smoothed version of \( q^{\text{int}}_{2,m=2} \) as defined by Ho and Rabitz.32 In the \( r \) direction we use the same functional form as for the \( \theta \) direction, \( q_3(z, z', \Delta z) \), with \( z(r) = 1 - \exp(-\beta r^2/2) \). In the \( r \) direction, we have used unsmoothed fitting functions, i.e., \( \Delta z = 0 \).

In each direction the set of raw fitting function, \( \{q(x, x', i); i = 1,...,N\} \), can be transformed into a set of orthogonal fitting functions by a canonical orthogonalization.34 Thus we define the matrix \( q_{ij} = q(x, x_i) \) and the matrix \( S \) is given by

\[
S = q^T q.
\]

We then diagonalize \( S \) by the unitary transformation \( U \) such that

\[
U^T SU = s,
\]

where \( s \) is a diagonal matrix. The canonical transformation matrix is then given by

\[
X = Us^{-1/2}.
\]

The orthogonalized fitting functions are then defined as

\[
\tilde{q}_{a,i}(x) = \sum_{j=1}^{N} q_{a,i}(x, x_j, \Delta x) X_{ji},
\]

where \( \alpha \) indicates the type of RKHS kernel used as indicated in Eqs. (2) and (4) above and the \( \Delta x \) is not explicitly part of the symbol used for the orthogonalized fitting function, \( q_{\alpha,i} \), but is implied. The three-dimensional orthogonalized fitting functions are then defined by

\[
Q_{ijk}(R, \theta, r) = \tilde{q}_{a,i}(R) \tilde{q}_{a,j}(y(\theta)) \tilde{q}_{a,k}(z(r)).
\]

We do not fit the potential \( V(R, \theta, r) \) directly, instead we fit a transformed potential \( \tilde{V}(R, \theta, r) \) defined by

\[
\tilde{V}(R, \theta, r) = \ln \left[ \frac{V(R, \theta, r) - V_{\text{lower}}}{V_{\text{lower}}} \right].
\]

The fitted potential is then defined as

\[
\tilde{V}_{\text{fit}}(R, \theta, r) = \sum_{ijk} C_{ijk} Q_{ijk}(R, \theta, r).
\]

The expansion coefficients \( C_{ijk} \) are obtained from the condition that the interpolation function matches the value of
intermolecular modes of the complex using an adiabatic or "Born–Oppenheimer-type" approximation.\textsuperscript{35,36} By making this separation, we are, in effect, averaging the intermolecular potential $V_{\text{int}}(R, \theta, r)$ over the HBr vibrational

states. We calculate the vibrational eigenvalues of $\hat{H}_{\text{mon}}(R', \theta')$ for HBr in the complex as a function of intermolecular coordinates $(R', \theta')$ using a modified Cooley approach.\textsuperscript{37} This is done on a grid of points $(R', \theta')$ in the center of mass coordinates.

The intermolecular Hamiltonian is then given by

$$H_{\text{int}} = -\left(\frac{\hbar^2}{2\mu R'} \frac{\partial^2}{\partial r^2} + \frac{j^2}{2I} + \frac{j^2}{2\mu R'^2} + V'(R', \theta')\right).$$

(16)

Here, $V'(R', \theta')$ represents the intermolecular potential of the whole complex averaged over the HBr or DBr vibrational states labeled by the vibrational quantum number $\nu$ and is given by the corresponding eigenvalue of $\hat{H}_{\text{mon}}(R', \theta')$. The moment of inertia of the diatom, $I$, in principle varies as a function of $(R', \theta')$ and is given by

$$I(R', \theta') = \mu' \left(\frac{1}{r^2} S_s(r; R', \theta')\right)^{-1},$$

(17)

where $S_s(r; R', \theta')$ are the eigenfunctions of $\hat{H}_{\text{mon}}(R', \theta')$, which depend parametrically on $R'$ and $\theta'$. The exact treatment of the $\frac{j^2}{2\mu R'^2}$ term in Eq. (14) would require the inclusion of the $R'$ and $\theta'$ dependence of $I$, as given in Eq. (17), and terms containing the first and second derivatives of $S_s(r; R', \theta')$ with respect to $\theta'$. However, the predicted values of the observables used in this study were found to be insensitive to the value of $I$ used and thus we chose to neglect these terms. The shifts in the observables were found to be at least an order of magnitude less than the uncertainties due to other approximations used in the calculation. This was evident when the value of $I$ was taken to be the value obtained from the intramolecular vibrational wave function found for the two different minima in the Ar:HBr surface. In practice, we chose the value of $I$ that was found for the intramolecular vibrational wave function at the HB minimum of the potential.

To compute the matrix elements of potential, $V''(R', \theta')$, the intermolecular potential was interpolated using the RKHS interpolation method discussed above with a two-dimensional kernel corresponding to the kernels used for the $R$ and $\theta$ degrees of freedom in the three-dimensional fit discussed previously. To evaluate the matrix elements of the potential, the interpolated potential $V''(R', \theta')$ was expanded in Legendre polynomials

$$V''(R', \theta') = \sum_{n=0}^{N_R-1} V_n(R') P_n(\cos \theta'),$$

(18)

and the expansion coefficients $V_n(R')$ were evaluated by numerical quadrature.

Following the method used previously, the VCI wave function for the intermolecular modes of the complex were calculated in three steps.\textsuperscript{38} First, a set of $N_R$ distributed Gaussian basis functions are chosen of the form

\[ C_{ijk} = \sum_{i'j'k'} Q_{ijk}(R_{i'}, \theta_{j'}, r_{k'}) \tilde{V}_{\text{ab initio}}(R_{i'}, \theta_{j'}, r_{k'}), \]
\[
\chi_i(R') = \left( \frac{2\alpha}{4\pi} \right)^{1/4} \frac{1}{R'} \exp \left[ -\alpha (R' - R_0)^2 \right].
\]  

(19)

With this set of Gaussians and using \( V'(R', \theta' = 0.0^\circ) \) as an effective radial potential, the one-dimensional radial Hamiltonian

\[
H_R = -\frac{\hbar^2}{2\mu R'} \left( \frac{\partial^2}{\partial R'^2} \right) R' + V_{\text{eff}}(R')
\]

(20)

was diagonalized to obtain a set of radial eigenfunctions \( C_i(R') \) expanded in the distributed Gaussian basis set \( \chi_i(R') \).

In the second step, a set of angular functions were obtained by diagonalizing the angular Hamiltonian

\[
H_{\text{ang}} = \frac{\hbar^2}{2I} \left( \sum_{\ell} C_i(R') \right) \left( \frac{\hbar^2}{2\mu R'^2} \right) R' + \sum_{\ell=0}^{N_o-1} V_{\ell}(R') P_{\ell}^j(\cos \theta') C_i(R') \),
\]

(21)

where \( C_i(R') \) was the lowest energy radial eigenfunction. This diagonalization is carried out in a set of coupled angular functions

\[
\Phi_{j,l}^{JM}(R', \hat{r}) = \sum_{m,j} \langle jlm,m_j|JM \rangle Y_{jm}(\hat{r}) Y_{jm}(\hat{r}'),
\]

(22)

where \( \langle jlm,m_j|JM \rangle \) are the Clebsch–Gordan coefficients. This leads to a set of optimized angular functions \( \Phi_{j,l}^{JM} \) that are linear combinations of the angular basis functions \( \Phi_{j,l}^{JM} \).

A new effective radial potential can then be obtained by averaging \( V'(R', \theta') \) over \( \Phi_{j,l}^{JM} \), the lowest eigenstate of \( H_{\text{ang}} \). The eigenvalue equations of the Hamiltonians \( H_R \) and \( H_{\text{ang}} \) were then iteratively solved until convergence of the lowest eigenvalues were obtained. This iterative procedure is known as the vibrational self-consistent-field (VSCF) method and yields a set of optimized angular and radial functions.

Finally, the total wave function \( \Psi^{JM} \) was evaluated as a linear combination of a product of the optimized radial and angular eigenfunctions

\[
G_{\lambda,i}^{JM}(R', \hat{r}) = \Phi_{j,l}^{JM}(R', \hat{r}) C_i(R')
\]

(23)

to give

\[
\Psi^{JM}(R', \hat{r}) = \sum_{\lambda,i} D_{\lambda,i}^{JM} G_{\lambda,i}^{JM}(R', \hat{r}).
\]

(24)

The expansion coefficients \( D_{\lambda,i}^{JM} \) were obtained by diagonalizing the intermolecular Hamiltonian. This form of wave function is known as a vibrational configuration interaction (VCI) wave function.

**D. Regularized potential morphing**

The PES obtained from the \textit{ab initio} potential gives fairly good agreement with the experimental results when it is employed to compute the rovibrational spectrum using the methods outlined in the preceding section. Here, we want to find a potential which gives much better agreement with the experimental results, and is, in some sense, close to the \textit{ab initio} PES. The method that has been used to construct such an improved potential is to fit the three-dimensional \textit{ab initio} potential using the RKHS method discussed above, then we constructed a transformed or morphed potential which is obtained from the \textit{ab initio} potential through the morphing transformation.

\[
V_{\text{morphed}}(R, \theta, r) = S_1(\theta, r) V_{\text{ab initio}}(S_2(\theta, r)(R - R_F)) + [1 + S_3(\theta, r)] R_F \theta, r,
\]

(25)

where \( R_F \) is a fixed point in the scaling transformation and where the morphing functions \( S_a \) are expanded in \( \theta \) and \( r \) as

\[
S_a(\theta, r) = \sum_{ij} C_{a,ij} P_i(\cos \theta) \left[ 1 - \exp \left( -\beta r - r_{e} \right) \right].
\]

(26)

In the current study, \( R_F \) was taken to be 3.9432 Å and \( \beta \) was taken to be 1.0. The introduction of \( R_F \) into the morphing transformation reduces the correlation between the \( S_2 \) and \( S_3 \) type parameters and thus accelerates the optimization procedure. The value of \( R_F \) chosen does not however change the final morphed potential. Note that in principle the morphing functions \( S_a \) should also depend on \( R \). However, we found that fitting the experimental data available for the Ar:HBr system did not require us to include such an \( R \) dependence in the morphing transformation.

Given the functional form of the morphed potential and a set of \( M \) experimental observables \( O_{\text{expt}} \) we then want to obtain the set of morphing expansion coefficients \( C_{a,ij} \) that give the best agreement between the observations \( O_{\text{expt}} \) and the predicted quantities \( O_{\text{calc}} \). Depending on the number of observations and the coefficients included in the expansion, this inversion process, i.e., obtaining a potential from a set of observables, can be ill conditioned. This can come from having more parameters than unknowns or from having near linear dependence among the parameters. In either case, the inversion process can be regularized by choosing an appropriate function to optimize. In the current application, we optimize the \( C_{a,ij} \) by minimizing the function

\[
F(C_{a,ij}, \gamma) = \sum_{k=1}^{M} \left( \frac{O_{k,\text{expt}} - O_{k,\text{calc}}(C_{a,ij})}{\sigma_k} \right)^2 + \gamma^2 \sum_{ij} \left( C_{a,ij} - C_{0,ij} \right)^2.
\]

(27)

In Eq. (27), \( \gamma \) is the regularization parameter, \( \sigma_k \) are the uncertainties in either the observed or computed values, and the \( C_{a,ij} \) are the values of the morphing parameters which correspond to no morphing, i.e., \( C_{a,ij}^{0} = 1 \). All others are zero. Minimizing \( F \) then yields a potential that simultaneously improves the agreement between the experimental and calculated observables and keeps the morphed potential close to the original \textit{ab initio} potential. The quality of the fit of the experimental data can then be characterized by the standard deviation of the fit

\[
\chi(\gamma) = \left[ \frac{1}{M} \sum_{k=1}^{M} \left( \frac{O_{k,\text{expt}} - O_{k,\text{calc}}(C_{a,ij})}{\sigma_k} \right)^2 \right]^{1/2}.
\]

(28)
the minimization of $F$ given in Eq. (27). Note that $\chi(\gamma=\infty)$ is just the quality of fit of the ab initio PES and $\chi(\gamma=0)$ would be the quality of fit for the unconstrained or “nonregularized” fit of the potential.

III. RESULTS AND DISCUSSION

A. Experimental and predicted observables

The experimental observables that we have fit are given in Table I. These data include information obtained from both microwave and IR experiments. All computed energy levels are given relative to the value of the adiabatic convention. In this convention, the quantum numbers $n$, $l$, and $J$ would be obtained from low-$J$ transitions and first and second differences of low-$J$ transition energies. Thus the rotational constants were calculated from the energy differences between two consecutive energy levels by

$$B[(v_1, v_2', v_3), J, J_{J-1}] = \frac{E[(v_1, v_2', v_3), J] - E[(v_1, v_2', v_3), J_{J-1}]}{2J}, \quad (29)$$

where $B[(v_1, v_2', v_3), J, J_{J-1}]$ is the rotational constant for a particular state $(v_1, v_2', v_3), J$, and $E[(v_1, v_2', v_3), J]$ and $E[(v_1, v_2', v_3), J_{J-1}]$ are the energies of two consecutive rotational energy states relative to the energy of corresponding monomer state with vibrational quantum $v_1$. By using a similar expression

<table>
<thead>
<tr>
<th>Observable</th>
<th>$Q_1^{calc}(\gamma=\infty)$</th>
<th>$Q_2^{calc}(\gamma=10.)$</th>
<th>$Q_3^{calc}$</th>
<th>Reference</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar:HBr ${E[(2,0,0), J] - E[(0,0,0), J]}$</td>
<td>13.57</td>
<td>11.07</td>
<td>11.08</td>
<td>12</td>
<td>0.04</td>
</tr>
<tr>
<td>Ar:HBr ${E[(1,1,0,0), J] - E[(0,0,0), J]}$</td>
<td>26.80</td>
<td>26.58</td>
<td>26.67</td>
<td>24, 12</td>
<td>0.04</td>
</tr>
<tr>
<td>Ar:HBr ${E[(1,0,0,0), J] - E[(0,0,0), J]}$</td>
<td>-0.806</td>
<td>0.330</td>
<td>0.337</td>
<td>12</td>
<td>0.013</td>
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<tr>
<td>Ar:HBr ${E[(2,0,0,0), J] - E[(0,0,0,0), J]}$</td>
<td>13.118</td>
<td>9.288</td>
<td>9.280</td>
<td>12</td>
<td>0.023</td>
</tr>
<tr>
<td>Ar:HBr ${E[(1,1,0,0), J] - E[(0,0,0), J]}$</td>
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<td>25.45</td>
<td>25.47</td>
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<td>0.05</td>
</tr>
<tr>
<td>Ar:HBr ${E[(1,0,0,0), J] - E[(0,0,0), J]}$</td>
<td>26.57</td>
<td>25.46</td>
<td>25.47</td>
<td>12</td>
<td>0.05</td>
</tr>
<tr>
<td>Ar:HBr ${E[(1,0,0,0), J] - E[(0,0,0), J]}$</td>
<td>21.46</td>
<td>25.70</td>
<td>25.75</td>
<td>12</td>
<td>0.12</td>
</tr>
<tr>
<td>Ar:HBr ${E[(2,0,0,0), J] - E[(0,0,0,0), J]}$</td>
<td>30.79</td>
<td>31.75</td>
<td>31.73</td>
<td>12</td>
<td>0.11</td>
</tr>
</tbody>
</table>

**TABLE I.** Experimental observables used to morph the Ar:HBr PES and their corresponding computed values.
where \( E_1^{(\lambda)} \) is the eigenvalue of the total operator, \( H = H^{(0)} + \lambda \hat{\chi} \), \( E_1^{(0)} \) is the corresponding eigenvalue of the unperturbed Hamiltonian \( H^{(0)} \), and \( O(\lambda) \) stands for the higher order perturbation terms. The calculated expectation values depend on the selection of the perturbing parameter \( \lambda \), which we have taken to be 0.01 cm\(^{-1}\) for both the \( P_1 \) and \( P_2 \) expectation values.

One additional experimental observable that we have included in our fitting procedure is \( D_{\theta} \), which is the \( \theta \) dependence of \( \langle P_2(\cos \theta') \rangle \), defined as

\[
D_{\theta} = \frac{1}{2} \left\langle (P_2(\cos \theta'))_{J-1} - (P_2(\cos \theta'))_{J-1} \right\rangle.
\]

There are a number of parameters used to define the calculations. As discussed above, we have chosen the rotational constants for the dimer that is used in Eq. (16) based on their value at the minimum in the adiabatic potential with \( \theta = 0^\circ \). The values used were 8.357 89 cm\(^{-1}\) for the Ar:HBr \( (v_1 = 0) \) complex, 8.143 83 cm\(^{-1}\) for the Ar:HBBr \( (v_1 = 1) \) complex, and 4.250 08 cm\(^{-1}\) for the Ar:DBr \( (v_1 = 0) \) complex. These can be compared to the values for the isolated HBr monomers which are 8.351 061(5) cm\(^{-1}\) for the HBr \( (v_1 = 0) \) monomer, \( 8.119 00(1) \) cm\(^{-1}\) for the HBr \( (v_1 = 1) \) monomer, and 4.248 1936(4) cm\(^{-1}\) for the DBr \( (v_1 = 0) \) monomer. The radial basis set as defined in Eq. (19) contained \( N_R = 50 \) Gaussian functions evenly distributed between 2.7 Å and 6.6 Å. In the expansion of the angular basis as given in Eq. (22), the maximum value of \( j \) was taken to be \( j_{max} = 14 \). All possible values of \( l \) were then included based on the value of \( J \) of the state and the value of \( j_{max} \). The number of terms included in the expansion of the potential was \( N_p = 20 \) as defined in Eq. (18). The grid of points \( (R', \theta') \), used to interpolate the two-dimensional adiabatic PES was taken as a direct product grid with 10 points in the \( R' \) direction starting at 3.1932 Å and ending at 5.4432 Å and with 10 points in the \( \theta' \) direction starting at 0° and ending at 180°. The value of \( V_{\text{lower}} \), as defined by Eq. (11), was \(-300 \) cm\(^{-1}\).

### Table II. Optimized morphing parameters \( C_{a,i,j} \) for \( \gamma = 10 \), and their corresponding uncertainties.

<table>
<thead>
<tr>
<th>( (a,i,j) )</th>
<th>( C_{a,i,j} (\gamma = 10) )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1,0,0)</td>
<td>1.1321</td>
<td>0.0489</td>
</tr>
<tr>
<td>(1,1,0)</td>
<td>0.0283</td>
<td>0.0042</td>
</tr>
<tr>
<td>(1,2,0)</td>
<td>0.0401</td>
<td>0.0110</td>
</tr>
<tr>
<td>(1,3,0)</td>
<td>-0.1289</td>
<td>0.0055</td>
</tr>
<tr>
<td>(1,4,0)</td>
<td>-0.0614</td>
<td>0.0107</td>
</tr>
<tr>
<td>(1,1,1)</td>
<td>-0.0397</td>
<td>0.0053</td>
</tr>
<tr>
<td>(2,0,0)</td>
<td>1.2503</td>
<td>0.0446</td>
</tr>
<tr>
<td>(2,1,0)</td>
<td>-0.0328</td>
<td>0.0148</td>
</tr>
<tr>
<td>(2,2,0)</td>
<td>-0.0456</td>
<td>0.0265</td>
</tr>
<tr>
<td>(2,3,0)</td>
<td>0.1954</td>
<td>0.0398</td>
</tr>
<tr>
<td>(3,0,0)</td>
<td>0.0506</td>
<td>0.0006</td>
</tr>
<tr>
<td>(3,1,0)</td>
<td>-0.0288</td>
<td>0.0017</td>
</tr>
<tr>
<td>(3,2,0)</td>
<td>-0.0164</td>
<td>0.0012</td>
</tr>
<tr>
<td>(3,0,1)</td>
<td>-0.0791</td>
<td>0.0036</td>
</tr>
<tr>
<td>(3,1,1)</td>
<td>-0.0761</td>
<td>0.0052</td>
</tr>
</tbody>
</table>

The uncertainties, \( \sigma \), given in Table I were taken to be the difference between the values of the various observables given in Table I when the parameters given above were used and the values of the observables when \( N_R = 55 \), \( j_{max} = 17 \), \( N_p = 25 \), and the two-dimensional PES grids were obtained at 12 points with the same range of \( R' \) and \( \theta' \). These uncertainties thus represent estimates of errors in the calculation due to lack of convergence of the numerical procedure used to obtain the eigenvalues of the intermolecular Hamiltonian. All of the errors were larger than the corresponding experimental uncertainties. The main source of the errors given in Table I is the dependence on the number of interpolation points. In principle, these errors could be made much smaller by calculating the ab initio potential at many more points so that the adiabatic potential could be obtained without interpolation at a fine grid of points which would then have a smaller interpolation error in the rovibrational eigenvalue calculation. We felt however, that the current approach gave adequate accuracy in light of the unknown errors introduced by the adiabatic treatment of the H–Br stretch and by the use of a particular approximate ab initio potential to form the basis of the morphed potential.

### B. Potential morphing

The problem of inverting experimental data to obtain a PES does not have a unique solution. Even within the procedure used here, there is no guarantee that the ‘‘best fit’’ found, for a given list of morphing parameters and experimental data, is the global minimum of the fitting function. The procedure we used was to fit the experimental data for the \( v_1 = 1 \) state of Ar:HBr with a set of morphing parameters which did not include any \( r \) dependence. We only retained parameters whose values were statistically significant. Thus if their statistical uncertainty were greater than \( C_{a,i,j} - C_{0,a,i,j} \) then that parameter was discarded. Once the \( v_1 = 1 \) state was fitted, the other data were included and morphing parameters describing the coupling to the \( r \) coordinate were included. These fits were done with a morphing parameter of \( \gamma = 10 \). In Table II we give the final list of morphing parameters used and the values obtained for these parameters for...
the $\gamma=10$ morphed potential. The value of the uncertainties, $\sigma$, given for the parameters in Table II are obtained from the propagation of the estimated values of $\sigma$ for the observables given in Table I. We have also considered how the morphing changed as a function of $\gamma$, the morphing parameter. In Fig. 1 we give the dependence of $\chi(\gamma)$ on $\gamma$. We can see that the standard deviation of the fit varies between $\chi(\gamma=\infty)=330.47$ and $\chi(\gamma=10)=1.50$.

The most interesting feature of Fig. 1 is that there is a break in the curve at approximately $\gamma=20-40$ such that lowering $\gamma$ does not lead to much further lowering of $\chi$. If one performs the optimization with $\gamma$ approaching 0, one finds that there is little further improvement in the fit of the experimental data. However in regions of the potential where there is minimal probability density in the experimentally observed state, the near linear dependence of the morphing parameters with small values of $\gamma$ leads to large deviations in the morphed potential compared to the original unmorphed $ab$ initio potential. Thus the most reliable morphed potential is obtained when the value of $\gamma$ is chosen as large as possible consistent with a good fit of the experimental data. The break in the $\chi$ vs $\gamma$ curve in Fig. 1 then indicates that a good choice for $\gamma$ is a value around 10–20. We have thus taken the potential obtained with $\gamma=10$, which had a standard deviation of $\chi=1.50$, as our best morphed potential.

In Table I we have also given the value of the experimental observable for the $ab$ initio potential ($\gamma=\infty$) and the morphed potential with $\gamma=10$.

C. Features of the morphed potential

In Fig. 2 we give three different two-dimensional cuts through the three-dimensional PES for Ar:HBr in the Jacobi coordinates for the Ar:HBr isotopomer. We show both the original $ab$ initio ($\gamma=\infty$) and the morphed PES ($\gamma=10$). Note that these plots are of $V^{int}$, the interaction potential of the HBr with the Ar. Thus the full PES would be the PES given in this figure plus the interaction potential for the HBr stretching mode for the isolated molecule as given in Eq. (1). The top two panels show the PES as a function of $R'$ and $\theta'$ for $r=r_e$. The shape of the potential does not change dramatically upon morphing, however there are some important differences. The $ab$ initio potential has a global minimum in the HB form with $V^{int}(R'=4.31\,\text{Å}, \theta'=0^\circ, r=r_e, (\text{fixed}))=-143.1\,\text{cm}^{-1}$ and a secondary minimum in the vdW form with $V^{int}(R'=3.82\,\text{Å}, \theta'=180^\circ, r=r_e, (\text{fixed}))=-136.6\,\text{cm}^{-1}$ where $r_e=1.4144\,\text{Å}$. In contrast to this, the morphed potential with $\gamma=10$ has the global minimum in $V^{int}$ with $r=r_e$ in the vdW form with $V^{int}(R'=3.59\,\text{Å}, \theta'=180^\circ, r=r_e, (\text{fixed}))=-165.4\,\text{cm}^{-1}$ and a secondary minimum in the HB form with $V^{int}(R'=4.20\,\text{Å}, \theta'=0^\circ, r=r_e, (\text{fixed}))=-144.5\,\text{cm}^{-1}$. Thus we find that in the HB structure, the morphed potential has the minimum at a distance which is 0.11 Å shorter than the $ab$ initio potential. The corresponding shift in the vdW structure is 0.23 Å. Thus both the structure and the well depth are more changed by the morphing in the vdW structure than in the HB structure. This change in the location and energy of the global minimum with morphing is also found in the adiabatic potentials for the three states of HBr considered here.

In the top two panels of Fig. 2, one sees some small amplitude wiggles in the plotted contours, especially in the region between 30° and 60°. These wiggles are due to a combination of the use of a relatively sparse grid and the use of a finite switching distance, $\Delta \gamma$, as defined by Eqs. (2) and (5) in the smoothed fitting functions. The smoothed fitting functions have been found to yield accelerated convergence of numerical integrals involving interpolated potentials since the smoothed functions do not have discontinuities in the higher derivatives. However, their convergence behavior is not as uniform as that found with the unsmoothed fitting functions.

One common way to understand the equilibrium distances in a given structure is by considering the sum of van der Waals radii of the atoms. Usually for light hydrides (HF and HCl) the H atom is considered to be contained inside the radius of the corresponding halogen. However, for HBr it has also been noted that the H atom extends beyond the van der Waals radius of the Br atom. Assuming that the H atom extends beyond the Br radius was previously found to be needed to fit the Ar:HBr potential. This assumption is also in agreement in the $ab$ initio and morphed potentials shown in the top panels of Fig. 2. In those panels the high curvature in the contours of the potential between 0° and 30° is due to the strong coupling between the $\theta'$ and $R'$ degrees of freedom as the H atom moves away from the intermolecular axis.

The other four panels shown in Fig. 2 show the dependence of $V^{int}$ as a function of $(R', r)$ with $\theta'=0^\circ$ and $180^\circ$. In both the $ab$ initio and morphed potentials we can see that in the HB geometry there is significant coupling between the $R'$ and $r$ coordinates. This coupling can also be interpreted using the sum of van der Waals radii. In the HB structure given in the middle two panels, the lengthening of the H–Br bond pushes the Br further away from the Ar. In the vdW...
FIG. 2. Comparison of the *ab initio* ($\gamma=\infty$) and morphed ($\gamma=10$) interaction potentials of Ar:HBr. For each potential three different cuts through the three-dimensional PES are given; $V^{\text{int}}(R',\theta',r=r_e)$, $V^{\text{int}}(R',\theta'=0^\circ,r)$, and $V^{\text{int}}(R',\theta'=180^\circ,r)$. All contours are given in cm$^{-1}$. Plots are in the Jacobi coordinates for the Ar:H$^7$Br isotopomer. The vertical dashed lines in the lower four panels are at $R_{\text{min}}^r$, the value of $R'$ at the local minima in the PES with $r=r_e$ and with the indicated value of $\theta'$. For $\gamma=\infty$ and $\theta'=0^\circ$, $R_{\text{min}}^r=4.31$ Å, for $\gamma=\infty$ and $\theta'=180^\circ$, $R_{\text{min}}^r=3.82$ Å, for $\gamma=10$ and $\theta'=0^\circ$, $R_{\text{min}}^r=4.20$ Å, and for $\gamma=10$ and $\theta'=180^\circ$, $R_{\text{min}}^r=3.59$ Å.
structures given in the bottom two panels, the lengthening of the H–Br bond does not lead to a lengthening of the Ar–Br distance since the H atom is not between the Ar and Br atoms so that the Ar–Br distance is only determined by the vdW radii of the Ar and Br atoms and not the position of the H atom. We also note that the lengthening the H–Br distance leads to a strengthening of the intermolecular interaction in both the HB and vdW structures.

In Table III we compare the energies of the HB and vdW rovibrational states for the \textit{ab initio} PES, the morphed PES, and the experiment for the three adiabatic PESs considered here. The reason that the minima in the PESs can have a different ordering than the corresponding rovibrational states is due to the differing zero-point energy in the different isomers. In Ar:Br, the vdW isomer is found to have a lower PES minimum but a higher rovibrational state energy compared to the HB isomer. Thus the zero-point energy in the vdW state must be larger than that in the HB state. We would then expect to find that such zero-point energy effects would be smaller in the case of the deuterium isotopes. This is indeed the case for both the \textit{ab initio} and morphed potentials considered here. In the case of the morphed potential, the difference in energy for the two isomers in the DBr case (5.63 cm\(^{-1}\)) is smaller than that in either of the HB states (10.99 cm\(^{-1}\) and 9.21 cm\(^{-1}\)). This substantial H–D isotope effect also indicates that this zero-point energy effect involves the bending mode rather than the intermolecular stretching mode. This can also be seen in the effective bending potentials shown in Fig. 3. The two curves in Fig. 3 correspond to the \textit{ab initio} and morphed Ar:HBr \((v_1=0)\) adiabatic potentials. These curves are the eigenvalues of Eq. (20) corresponding to the lowest stretching state at each value of \(\theta'\) for each adiabatic potential where we have taken \(V_{\text{eff}}(R')=V(R',\theta')\). We can see that the curvature of the potential for the bending motion is less in the HB region of the potential than in the vdW region of the potential.

Although it is not possible to obtain an absolute error estimate for our morphed potentials, it is possible to compute an error estimate within the assumed functional form. In Fig. 4, we give this error estimate for the morphed potential for the same three cuts through the potential as were given in Fig. 2. The error given in Fig. 4 is the mean deviation of the potential from its value obtained with the optimized parameters relative to the value at the HB minimum, as given in Fig. 2, for all variations of the morphing parameters such that the value of \(F\), as defined in Eq. (27), is twice as large as its optimum value. The results in the top panel show that the procedure used here, combining potential morphing and regularized inversion, leads to a well defined inverted potential with less than 5 cm\(^{-1}\) uncertainties over large ranges of the coordinates. This is in contrast to the unregularized fitting of an empirical PES functional form\(^{18}\) which lead to small errors only in the region of the potential for which there was substantial probability density in the states observed experimentally.

One quantity that has not yet been determined experimentally is the value of \(D_0\). In previous studies of the Ar:HBr potentials\(^{4,12}\) the well depth of the potential has been fixed by using a value of \(-111.3\) cm\(^{-1}\) for the minimum value of the potential with \(\theta'=90^\circ\) that had been estimated from the strength of the asymptotic van der Waals interaction in the Ar:HBr complex and the well depths of other Rg:HX complexes.\(^{10}\) The value we obtain in this study for the minimum value of the potential with \(\theta'=90^\circ\) was \(-87.8\) cm\(^{-1}\).

![Fig. 3. The effective bending potential for Ar:HBr \((v_1=0)\) including the zero-point energy in the \(r\) and \(R'\) degrees of freedom. This potential is the eigenvalue of Eq. (20) corresponding to the lowest stretching state at each value of \(\theta'\). The solid line is from the morphed \((\gamma=10)\) potential and the dashed line from the \textit{ab initio} \((\gamma=\infty)\) potential.](image-url)
state of the HBr monomer. The present potential is somewhat shallower than the previous estimate. The methods used in the current study do not fix the absolute well depths with any certainty, however the values of the potential relative to the minimum value are more certain.

We also see in Table I that the \textit{ab initio} PES does not predict the blueshift of 0.336 65 cm\(^{-1}\) found experimentally for the \(\nu_1\) fundamental relative to its value in the free HBr molecule. The \textit{ab initio} potential does however find that the vdW isomer has a corresponding redshift close to the observed\(^{12}\) redshift of 1.460 95 cm\(^{-1}\), as indicated in Table III. In Fig. 5 we show cuts through the two-dimensional adiabatic PESs for Ar:HBr (\(\nu_1=0\)) and Ar:DBr (\(\nu_1=1\)) with the corresponding cuts through the three-dimensional PES with \(r=r_e\). We can see that at the vdW geometry the excitation of the HBr stretch makes the well somewhat deeper without any noticeable shift in the value of \(R'\) at the minimum of the well. This is seen to be true in both the \textit{ab initio} and morphed potentials. This shift in the adiabatic potential is due to two factors: the anharmonicity of the HBr stretching motion which leads to a slightly larger probability density in the vibrational wave function at \(R>r_e\) in the \(\nu_1=1\) state compared to the \(\nu_1=0\) state; and the fact that the interaction potential become more attractive as \(r\) increases which can be seen in both potentials in Fig. 2. At the HB geometry the effects of the excitation of the HBr stretch are different in the \textit{ab initio} and morphed adiabatic PESs. In both potentials the value of \(R'\) at the minimum of the well becomes larger as the HBr bond length becomes larger. However in the morphed potential the value of the potential at the minimum in the HB structure increases in energy as \(r\) becomes larger whereas in the \textit{ab initio} potential the value of the potential at the minimum decreases. This difference between the two potentials is due to the changes seen in the fixed \(\theta'=0^\circ\) panels in Fig. 2. The \textit{ab initio} (\(\gamma=\infty\)) potential has a lower curvature in the \(R'\) direction than the morphed (\(\gamma=10\)) potential. Thus at the minimum in the \textit{ab initio} potential with \(\theta'=0^\circ\) and \(r=r_e\), i.e., at \(R'=4.31\) Å as indicated by the vertical dashed line in Fig. 2, the \textit{ab initio} potential is only decreasing as \(r\) increases in the range of \(r\) plotted. In contrast to this, at the minimum in the morphed potential with \(\theta'=0^\circ\) and \(r=r_e\), i.e., at the \(R'=4.20\) Å as indicated by the vertical dashed line, the morphed potential decreases slightly then increases as \(r\) increases beyond \(r_e\). This increase in the PES with increasing \(r\) leads to the positive energy shifts in the adiabatic potentials seen in Fig. 5.

IV. CONCLUSIONS

We have extended the method of morphing an \textit{ab initio} potential to represent weakly interacting molecular complexes to three dimensions including the coupling of intramolecular and intermolecular modes. This approach combined with a regularization procedure used to constrain the morphing process leads to a method that avoids the difficulties associated with the near linear dependence of morphing parameters.
We have applied this method to the three-dimensional structure of the Ar:HBr PES where the HBr stretch was treated using an adiabatic approximation. We have found that the morphed potential for the Ar:HBr system has a global minimum in the vdW structure and a secondary minimum in the HB structure. In contrast to the underlying potential, the ground rovibrational state is found to be the HB structure. This was true for all three of the adiabatic PESs \( n_1 = 0, \) \( n_1 = 1, \) and \( n_1 = 0 \) considered here.

We have also seen that the \textit{ab initio} PES more accurately represents the \( R-r \) coupling in the vdW region of the potential than in the HB region of the potential.

The results presented here suggest that for weakly interacting hydrogen bound systems, the distinction between the minimum in a PES and the vibrationally averaged structure of the ground state can be quite important. There have been extensive \textit{ab initio} calculations involving hydrogen bound complexes in the literature for which it has been implicitly assumed that the global minimum structure of such interactions are identical to the ground vibrational state structure. An effect similar to that found in the Ar:HBr complex has been observed previously for the weakly bound He:Cl\(_2\) complex involving linear and T-shaped isomers.\(^{26}\) In the current study such observations have been extended to interactions involving HBr, a proton donor capable of forming hydrogen-bound complexes. We do not consider these results to be unique and the effect is far more widespread than previously suspected without consideration of the relevant dynamics. Current experimental studies of relatively simple systems such as HeCl\(_2\) and Ar:HBr, indicate potential limitations of such approaches, specifically in more complicated interactions that have not been the subject of detailed spectroscopic and dynamical analysis. We consider this to be particularly true for the modeling of many biochemically significant in-

FIG. 5. Comparison of the \textit{ab initio} \((\gamma = \infty)\) and morphed \((\gamma = 10)\) adiabatic PES of Ar:HBr \((n_1 = 0)\) (dashed line), Ar:HBr \((n_1 = 1)\) (dashed–dotted line), and the \( r=r_e \) slice of the three-dimensional PES of Ar:HBr (solid line) at the HB structure \((\theta' = 0^\circ)\) and vdW structure \((\theta' = 180^\circ)\).
interactions where the opportunities exist for many almost equienergetic isomeric forms to coexist such as would be expected in models for peptide bonds and their solvated equivalents.

ACKNOWLEDGMENTS

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2 Molecular Interactions: From van der Waals to Strongly Bonded Complexes, edited by S. Scheiner (Wiley, Chichester, 1997).
41 See EPAPS Document No. E-JCP86-115-016126 for a copy of the program that computes the morphed three-dimensional potential for Ar:HBr, a sample input file, and a sample output file. The material deposited in the EPAPS also includes, in the sample input file, the computed ab initio interaction energies for this system. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory epaps. See the EPAPS homepage for more information.