Adiabatic three-dimensional simulations of the IHI⁻, BrHI⁻, and BrHBr⁻ photoelectron spectra

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In order to better characterize the transition-state region for the I + HI, Br + HI, and Br + HBr reactions, the photoelectron spectra of IHI^- , IDI^- , $BrHI^-$, $BrHBr^-$, and $BrDBr^-$ have been simulated using a three-dimensional adiabatic approach. This method of simulation uses a Born–Oppenheimer separation in time scales between the fast hydrogen-atom motion and the slow halogen-atom motion to greatly simplify the computation of the photoelectron spectrum. The resulting simulations are compared to the experimental photoelectron and threshold photodetachment spectra of these anions, and to "exact" simulations of the IHI⁻ and IDI⁻ spectra. The comparison with the exact simulations shows that the adiabatic method is reasonably accurate, and is a considerable improvement over previous approximate simulation schemes. Potential-energy surfaces for the I + HI and Br + HI reactions are evaluated based on a comparison between the simulated and experimental spectra. A three-dimensional surface for the Br + HBr reaction that reproduces the experimental photoelectron spectrum is constructed by extending a fitted collinear surface to three dimensions.

I. INTRODUCTION

The characterization of the transition-state region of the potential-energy surface for a chemical reaction has been a long-standing goal of chemical dynamics.¹ The transition-state region intimately affects the observable features (reaction rate, product energy, and angular distributions, etc.) of a chemical reaction. Recently, a variety of experiments² have been performed that seek to directly spectroscopically probe the transition-state region of a chemical reaction. In our group we use one of these methods, negative-ion photodetachment, to study the transitionstate region of neutral bimolecular reactions. In these experiments, photodetachment of a stable negative ion is used to access the transition state of a bimolecular reaction in a controlled manner. If the negative-ion precursor is similar in structure to the transition state for the neutral reaction, the photoelectron spectrum will contain detailed information on the transition-state region of the neutral potentialenergy surface. In this manner, we have studied the potential-energy surface for the hydrogen transfer reactions $X + HY \rightarrow XH + Y$ by obtaining the photoelectron spectra or the higher-resolution threshold photodetachment spectra of the bihalide anions XHY-, where X and Y are like³⁻⁷ or unlike^{7,8} halogen atoms.

These spectra show resolved vibrational structure associated with the unstable XHY complex formed by photodetachment. Some of these peaks are due to transitions to relatively long-lived XHY states; these states are the origin of the sharp reactive resonances seen in scattering calculations on X + HY reactions.⁹⁻¹³ However, most of the observed structure consists of broad peaks due to overlap with nonresonant, direct scattering states on the neutral potential-energy surface.⁵ Both the resonant and directscattering features contain information on the potentialenergy surface for the neutral reaction.

Ideally, one wishes to use the photoelectron spectra to characterize that region of the potential-energy surface which has good Franck-Condon overlap with the negative ion. A method for inversion of the spectra has yet to be developed, so at this point the most promising approach appears to be an iterative one, in which the photoelectron spectrum is simulated assuming a particular neutral potential-energy surface and anion geometry. The neutral potential is then modified and the procedure is repeated to obtain improved agreement with experimental results. This procedure requires an accurate, efficient method of simulating the photoelectron spectrum. Several theoretical approaches have been developed for simulating these spectra. The most sophisticated of these are the "exact" simulations of the $IHI^{-,13-16}$ $IDI^{-,17}$ and $ClHCl^{-}$ (Refs. 12, 18, and 19) spectra by Schatz, and of the FH_2^- spectrum by Miller and co-workers,²⁰ in which the Franck-Condon overlap between the anion and the full three-dimensional neutralscattering wave functions (with total angular momentum J=0) is calculated as a function of energy. However, these methods are too time consuming for an iterative approach. On the other hand, the collinear simulations used by us^{4,5,7,8} and the reduced dimensionality and threedimensional L^2 approaches developed by Bowman and coworkers²¹⁻²³ do not reproduce some of the key features seen in the experimental spectra. In this paper, we describe an approximate three-dimensional simulation scheme, based on the ideas of Manz and co-workers,^{24,25} Pollak,²⁶ and Kubach,²⁷ which provides a reasonable compromise between speed and accuracy.

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FIG. 1. Experimental photoelectron spectra of IHI^- obtained using the fixed-frequency photoelectron spectrometer (---), and higher-resolution spectra obtained using the zero-electron kinetic-energy (ZEKE) spectrometer (---). The peak heights in the ZEKE spectra have been scaled to those obtained using the fixed-frequency spectrometer and the peaks have been shifted by 7 meV.

The range of features one needs to be able to reproduce in a simulation is exemplified in Fig. 1, which shows the photoelectron spectrum⁴ superimposed on the IHIhigher-resolution threshold photodetachment spectrum.⁶ The peaks are labeled by the antisymmetric stretch v_3 quantum number of the neutral IHI complex. The threshold photodetachment spectrum shows that the $v_3 = 2$ and $v_3 = 4$ features consist of progressions of narrow peaks spaced by about 100 cm^{-1} . On the basis of collinear simulations⁷ and Schatz's three-dimensional (J=0) scattering simulations¹³⁻¹⁵ of the photoelectron spectrum, we have assigned these features to resonance states supported by the potential-energy surface for the I + HI reaction. In contrast, the $v_3 = 0$ manifold consists of a series of fairly broad peaks. On the basis of the peak spacings, these were assigned to hindered rotor states of the [IHI] complex in which the hydrogen atom orbits each of the iodine atoms. These "rotational threshold" features appear in the threedimensional scattering simulations of Schatz, but are not reproduced in collinear simulations. However, the overall appearance of the $v_3 = 0$ feature in Schatz's simulated spectrum is quite different from the experimental feature, and the $v_3 = 2$ resonances are much narrower in the simulated than experimental spectra. These discrepancies are presumably due to deficiencies in the I + HI surface²⁴ used in the simulations.

In order to ultimately obtain an improved potentialenergy surface, it would be useful to have an approximate three-dimensional method that can reproduce all the features observed in the spectrum, yet is much less computationally demanding than the full scattering calculation. One likely candidate is an adiabatic three-dimensional approach. This is based on treatments^{11,24–28} of the collinear heavy + light-heavy systems which showed that the fast hydrogen-atom motion and slow halogen-atom motion are separable to a good approximation; the mathematics of this are analogous to the Born–Oppenheimer approximation in diatomic molecules. In the transition-state region for the I + HI reaction, the H-atom and I-atom vibrations correspond to the antisymmetric and symmetric stretches, respectively, of the IHI complex. Within this collinear adiabatic approximation, one can construct a set of vibrationally adiabatic curves which show how the energies of the IHI antisymmetric stretch levels vary with interiodine distance; in the asymptotic region, these curves correlate to various I + HI(v, j=0) levels. Simulations of XHX⁻ spectrum within this collinear adiabatic approximation agreed extremely well with full two-dimensional wave-packet calculations.⁷

This adiabatic approach has been extended to three dimensions by Kubach,²⁷ who has carried out calculations extending the Born-Oppenheimer-type separation of time scales to three dimensions; the slow symmetric stretch is assumed to be separable from the two fast H-atom vibrations, the bend and antisymmetric stretch. At each value of the scattering coordinate (the interiodine distance) the two-dimensional Schrödinger equation for hydrogen-atom motion is solved to find the bend and antisymmetric stretch eigenvalues. This generates a complex set of "bendstretch" adiabatic curves which correlate asymptotically to various I + HI(v, j) levels. Kubach then couples these adiabatic curves approximately to form a set of diabatic curves which provide considerable insight into the quantum dynamics of the I + HI reaction. Very recently, Grayce and Skodje²⁹ implemented a somewhat different adiabatic scheme for the I + HI reaction in which they calculate two-dimensional adiabatic surfaces which show how the energy of each antisymmetric stretch level varies with interiodine distance and bond angle.

In this paper, we take Kubach's three-dimensional (3D) adiabatic approach in a somewhat different direction and use it to simulate the photodetachment spectra of IHI⁻ (and several other anions). For a given potentialenergy surface, we generate a set of H-atom bend-stretch adiabatic curves as a function of interiodine distance. Scattering wave functions are then found on these adiabatic curves and their overlap with the anion wave function is calculated in order to simulate the IHI⁻ photoelectron spectrum. Comparison with the exact results of Schatz¹⁵ shows that the adiabatic three-dimensional method is a significant improvement over the collinear calculations, while requiring significantly less computational effort than the full 3D scattering calculation. A full description of the adiabatic three-dimensional method is given in Sec. II. Our results on IHI⁻ and IDI⁻ photodetachment using the LEPS-A surface²⁴ for the I + HI reaction are compared to the exact scattering results of Schatz in Secs. III A and III B. In the remainder of Sec. III we apply our method to the analysis of several less-well-characterized systems: IHI⁻ and IDI⁻ using the more repulsive LEPS-C potential, which Schatz et al. have studied over a limited energy range;¹⁶ BrHI⁻, for which only collinear simulations were previously available;⁸ and BrHBr⁻ and BrDBr⁻ using a fitted potential surface, extending our earlier collinear work on this system.⁵ Conclusions are presented in Sec. IV.

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TABLE I. Negative-ion frequencies and geometries used in simulations.

Molecule (XHY ⁻)	$\frac{v_1^{a}}{(cm^{-1})}$	v_2^{b} (cm ⁻¹)	v_3^{a} (cm ⁻¹)	R _{eXY} (Å) ^b	R _{eXH} (Å) ^b	D ₀ ^c (eV)	A ^d (eV)
BrHBr-	164	700	728	3.50	1.75	0.906	1.717
BrDBr ⁻	170	500	498	3.50	1.75	0.898	1.678
BrHI ⁻	100 ^e	700	920 ^e	3.88	1.55	0.698	2.231
IHI-	121	700	682	3.88	1.94	0.737	1.006
IDI -	124	495	470	3.88	1.94	0.735	0.967

^aFrom Ref. 30, except where noted.

^bEstimates, except where noted.

^cValues of D_0 are from Ref. 49 and have an uncertainty of 0.05 eV. Values of D_0 for deuterides are calculated using D_0 for the hydride and correcting for zero-point energy using the above frequencies for XH(D)Y⁻ and the known frequencies of H(D)Y.

 ${}^{d}A$ is the conversion from scattering energy to electron kinetic energy: SE=A - eKE; see text.

^eA Morse oscillator with $\omega_e = 1276.3 \text{ cm}^{-1}$ and $\omega_e x_e = 178.1 \text{ cm}^{-1}$ is used for BrHI⁻. Harmonic oscillators are used for all other modes.

II. METHOD

In this section, we discuss the adiabatic threedimensional method of calculating the photoelectron spectrum and give details on our implementation of this method. We simulate the spectrum within the Franck-Condon approximation, so the intensity of a peak at energy E is given by the Franck-Condon factor

$$I \propto \left| \left\langle \Psi_0^i \middle| \Psi^f(E) \right\rangle \right|^2,\tag{1}$$

where Ψ_0^i is the initial anion wave function (assumed to be the vibrational ground state) and $\Psi^f(E)$ is the scattering wave function on the neutral surface with energy *E*. Simulating the spectrum thus consists of calculating the v=0anion wave function and the neutral wave function as a function of energy and determining this overlap.

Experimental information on the anions is somewhat limited, as there is no gas-phase spectroscopic information on any of the anions in this study, although some vibrational frequencies have been determined in a matrix.³⁰ The parameters used in our simulations for each negative ion are given in Table I. The anion potentials are assumed to be separable along all three directions. For BrH(D)Br⁻ and $IH(D)I^{-}$ we use harmonic potentials with the matrixisolation frequencies for the symmetric stretch (v_1) and antisymmetric stretch (v_3) , and a harmonic bend (v_2) potential with a frequency of 700 (495) cm^{-1} for IHI⁻ (IDI⁻). These are the same parameters as were used in all of the earlier simulations of the IHI- and IDI- spectra^{4,13–15,17,21,22} and allow comparison of the results. For BrHI⁻ we use a Morse potential fit to the v_3 matrixisolation frequencies³⁰ for BrHI⁻ and BrDI⁻; this is the same stretching potential as was used in our earlier collinear study.⁸ We use the same value of v_2 for BrHI⁻ and BrHBr⁻ as for IHI⁻, in the absence of experimental data. The simulations are very sensitive to the anion geometry. IHI⁻ and BrHBr⁻ are thought to be linear and centrosymmetric, but the interhalogen distance has not been experimentally determined in the gas phase for any of the systems described here. The values used are based on educated guesswork with (in the case of BrHBr⁻) some



FIG. 2. Polar coordinate system. See text for an explanation of the coordinates.

guidance from *ab initio* calculations.³¹ The geometry of BrHI⁻ is the same as was used in our earlier collinear study. We use semiempirical LEPS potential surfaces³² for the I + HI and Br + HI reactions. For the Br + HBr reaction we will use a fitted semiempirical potential, described in Sec. III E.

We now define the coordinates we use to describe the motions of the three atoms. The potentials for these systems all have cylindrical symmetry, so cylindrical coordinates (Fig. 2) are used to exploit this symmetry. The halogen atoms are taken to lie on the z axis, evenly spaced³³ about z=0 and separated by R. The hydrogen-atom position is specified by (ρ,z,ϕ) , where ρ is the distance from the z axis and ϕ is the azimuthal angle. The volume element is $d\tau = \rho \ d\rho \ dz \ d\phi$.³⁴ The Hamiltonian is then

$$H = T_{H}(\rho, z, \phi) + T_{X}(R) + V(\rho, z, R),$$
(2)

where T_H is the hydrogen kinetic energy, T_X is the kinetic energy of the halogen atoms, and V is the potential. We denote the solutions to this Hamiltonian $\Psi(\rho, z, \phi, R)$. We now make the adiabatic approximation^{5,11,27,35} and write

$$\Psi(\rho, z, \phi, R) = \Delta(R) \Gamma(\rho, z, \phi; R), \qquad (3)$$

where the wave functions for hydrogen-atom motion $\Gamma(\rho,z,\phi;R)$ change slowly with R and are found by solving the Schrödinger equation with the Hamiltonian for hydrogen-atom motion,

$$H_H = T_H(\rho, z, \phi) + V(\rho, z, R), \qquad (4)$$

at fixed R to find the eigenvalues $U_k(R)$. The hydrogen motion eigenvalues $U_k(R)$ form effective potentials (adiabatic curves) that govern the motion of the halogen atoms, analogous to the nuclear potential curves that are formed by solving the electronic Schrödinger equation in the Born–Oppenheimer approximation.^{5,11} Once we have the adiabatic curves, the wave functions $\Delta(R)$ for motion of the halogen atoms are found by solving the onedimensional Schrödinger equation with the heavy-atom Hamiltonian

$$H_{\chi} = T_{\chi}(R) + U_k(R). \tag{5}$$

Bound, quasibound, and scattering wave functions $\Delta(R)$ are found on each of the adiabatic curves and their Franck-Condon overlap with the anion ground state is determined. The method we use to solve the Hamiltonian for hydrogen-atom motion will now be described in some detail.

The Schrödinger equation for hydrogen-atom motion at fixed R, in atomic units, is³⁴

$$\left[-\frac{1}{2\mu}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}+\frac{\partial^2}{\partial z^2}\right)+V(\rho,z)\right]\Gamma_{k,l}(\rho,\phi,z)$$
$$=U_{k,l}\Gamma_{k,l}(\rho,\phi,z).$$
(6)

As the potential is independent of ϕ , we can make the substitution

$$\Gamma_{k,l}(\rho,\phi,z) = \Xi_k(\rho,z)\Phi_l(\phi), \tag{7}$$

where

$$\Phi_l(\phi) = (2\pi)^{-1/2} e^{il\phi}, \tag{8}$$

where l=0 (σ), ± 1 (π),.... We need only calculate σ states, as the v=0 XHY⁻ wave function has l=0 and so will only have Franck-Condon overlap with l=0 states on the neutral surface. The Schrödinger equation for l=0 is

$$\left[-\frac{1}{2\mu}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{\partial^2}{\partial z^2}\right)+V(\rho,z)\right]\Xi_k(\rho,z)=U_k\Xi_k(\rho,z).$$
(9)

We then make the change of variables $r = \rho^2/2$ to make the volume element $d\tau = dr dz d\phi$. The Schrödinger equation for hydrogen motion is now

$$\left[-\frac{1}{2\mu}\left(2r\frac{\partial^2}{\partial r^2}+2\frac{\partial}{\partial r}+\frac{\partial^2}{\partial z^2}\right)+V(r,z)\right]\Xi_k(r,z)$$
$$=U_k\Xi_k(r,z).$$
(10)

The Schrödinger equation is solved using a product basis consisting of harmonic oscillators: a one-dimensional harmonic oscillator along the hydrogen stretching coordinate z and the radial portion of a two-dimensional harmonic oscillator with l=0 along the bending coordinate r. These are the exact solutions of H_H for the potential $V_{ref}(r,z)$ $= k_r r + k_z z^2/2$ with energy levels

$$E_{m,n} = (k_r/\mu)^{1/2} (m+1) + (k_z/\mu)^{1/2} (n+\frac{1}{2}).$$
(11)

The basis-set frequencies $(k_r/\mu)^{1/2}$ and $(k_z/\mu)^{1/2}$ are chosen for optimum convergence of the calculation (see below). The eigenfunctions $X_{m,n} = R_m(r)Z_n(z)$ are well known.³⁶

As we are using an orthonormal product basis, we can use the discrete variable representation (DVR) to easily and efficiently evaluate matrix elements of the Hamiltonian. DVR methods have been applied to many systems with large-amplitude motions, including reactive scattering problems^{37,38} and vibrations of floppy molecules.^{39,40} The method has been thoroughly described by Light, Hamilton, and Lill⁴¹ and our application of it has been discussed in detail elsewhere.⁴²

Briefly, the Hamiltonian is rewritten as

$$H_H = H_{\text{ref}} + \Delta V(r, z), \qquad (12)$$

where

and

$$H_{\rm ref} = T_H(r,z) + V_{\rm ref}(r,z)$$
(13)

 $\Delta V(r,z) = V(r,z) - V_{\text{ref}}(r,z). \tag{14}$

We then find the matrix elements of H_H in an appropriate finite coordinate representation (the DVR) using the following procedure. We first require the eigenvalues and eigenvectors of the position matrix X in the $Z_n(z)$ and $R_m(r)$ bases. For the one-dimensional harmonic oscillator, the matrix elements are⁴³

$$X_{n,n'} = \langle Z_n(z) | z | Z_{n'}(z) \rangle$$

= $(n/2)^{1/2} \delta_{n,n'+1} + [(n+1)/2]^{1/2} \delta_{n,n'+1}.$ (15)

The matrix X is diagonalized to obtain eigenvalues z_n and the eigenvector matrix \mathbf{T}_{z} . Similarly, we obtain eigenvalues r_m and eigenvectors \mathbf{T}_r by diagonalizing⁴⁴

$$X_{m,m'} = \langle R_m(r) | r | R_{m'}(r) \rangle$$

= $\frac{m}{2} \delta_{m,m'+1} + \frac{2m+1}{2} \delta_{m,m'} + \frac{m+1}{2} \delta_{m,m'-1}.$ (16)

We also require the matrices K_z and K_r which are given by

$$K_z = T_z^T E_z T_z, \quad K_r = T_r^T E_r T_r$$
(17)

where E_z and E_r are the diagonal matrices of eigenvalues for the reference potentials in z and r, respectively [Eq. (11)]. The matrix elements of the Hamiltonian in the DVR are then given by³⁹

$$H_{mn,m'n'} = (K_z)_{n,n'} \delta_{m,m'} + (K_r)_{m,m'} \delta_{n,n'} + \Delta V(r_m, z_n) \delta_{m,m'} \delta_{n,n'}.$$
 (18)

The Hamiltonian matrix is diagonalized to obtain all the bend-stretch energies U_k at a particular interhalogen distance.

The DVR method evaluates the kinetic-energy term in the Hamiltonian exactly. The potential-energy terms are found approximately by evaluating the potential difference ΔV at the DVR points (r_m, z_n). This is equivalent to approximating the matrix elements of the potential difference

$$\langle \Xi_{m,n} | \Delta V | \Xi_{m',n'} \rangle = \int dr \int dz \, \Xi_{m,n}(r,z)$$

$$\times \Delta V(r,z) \Xi_{m',n'}(r,z),$$
(19)

using an $N_r \times N_z$ point Gaussian quadrature,⁴⁵ where N_r is the number of basis functions in r and N_z is the number in z. This procedure is extremely efficient, as no integrals are actually computed to construct the Hamiltonian matrix; constructing the Hamiltonian matrix requires diagonalizing a $N_r \times N_r$ matrix, a $N_z \times N_z$ matrix, and evaluating the potential at N_rN_z points. Once the Hamiltonian matrix is constructed, the computational problem consists of determining the eigenvalues and eigenvectors of a large, sparse matrix, which is ideally suited to the use of vector computers.

The potential energy is only determined approximately, so the DVR is not variational—the eigenvalues found are not strict upper bounds to the true eigenvalues.⁴¹ However, eigenvalues found using the DVR are very accurate and quickly converge to the true answer as the size of

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the basis is increased. For symmetric systems, the wave functions are either symmetric (gerade) or antisymmetric (ungerade) about z=0. Only gerade states on the neutral potential-energy surface will have Franck-Condon overlap with the symmetric v=0 anion wave function, so the basis set consists of only even functions $Z_n(z)$ for symmetric systems.

The harmonic basis we use is very well suited to geometries where all three atoms are interacting strongly, and this is the portion of the potential that the experimental results are most sensitive to. Unfortunately, this basis is not well suited to the asymptotic region, where we have free HX interacting weakly with X. As we wish to determine what product state each adiabatic curve correlates to, we must adequately describe the asymptotic region, and this requires large basis sets. The number of basis functions along each coordinate N_R and N_z and the basis-set frequencies $\tilde{\omega}_r = (k_r/\mu)^{1/2}$ and $\tilde{\omega}_z = (k_z/\mu)^{1/2}$ are chosen by solving Eq. (10) at large R and varying the number of basis functions and their frequencies until the eigenvalues U_k are insensitive to N_n N_n ω_n and ω_r . For the IHI⁻ and IDI⁻ simulations, good convergence of the first 50 eigenvalues is achieved with $N_r = 24$ and $N_z = 45$ (corresponding to even basis functions in z, up to a quantum number of 90, and 1080 basis functions in all), with $\omega_r = 800 \text{ cm}^{-1}$ and ω_z = 180 cm⁻¹ for IHI⁻ and ω_r = 350 cm⁻¹ and ω_z = 120 cm⁻¹ for IDI⁻. Good convergence of the first 30 eigenvalues for the asymmetric BrHI⁻ system requires $N_r = 18$ and $N_z = 78$ (1404 basis functions) with $\omega_r = 800 \text{ cm}^{-1}$ and $\omega_z = 190 \text{ cm}^{-1}$. [The same basis is then used to solve Eq. (10) at all R and is also used to solve Eq. (10) for the anion.] For comparison, Kubach²⁷ and Schatz¹⁴ use an "asymptotic basis" consisting of slightly modified rovibrational states of HX as their basis and achieve good convergence with only <75 basis functions. The asymptotic basis is not orthonormal, so it must be orthonormalized, and determining matrix elements of the Hamiltonian requires integrating over the potential. Although the adiabatic DVR method uses a very large basis, the method is very efficient. Constructing adiabatic curves for the Br + HBr system takes 5 CPU minutes on a Cray X-MP/14 and the full simulation takes 7 CPU minutes.

Wave functions $\Xi_k(\rho, z; R)$ and eigenvalues $U_k(R)$ for hydrogen-atom motion are found at 40 values of the interhalogen distance R to form adiabatic effective potential curves for the halogen motion. Each adiabatic curve $U_k(R)$ asymptotically correlates to a particular state of X + HY(v, j). Many such curves are responsible for the structure observed in the experimental photoelectron spectrum. For IHI⁻ some 60 adiabatic curves [correlating to I + HI (v=0, j=0-27; v=1, j=0-20; v=2, j=0-10)] must be considered; they are shown in Fig. 3(a). Once the adiabatic curves have been determined, they could be coupled exactly (which would be equivalent to Schatz's scattering calculation) or approximately (as has been done by Kubach in his diabatic calculation). In our adiabatic calculation we ignore the coupling and treat each adiabatic curve separately.



FIG. 3. (a) Three-dimensional adiabatic curves of σ_g symmetry for the I + HI system on the LEPS-A potential. Each curve correlates to I + HI(v, j). (b) Collinear adiabatic curves of gerade symmetry for the I + HI system on the LEPS-A potential, including zero-point bend. Each curve correlates to I + HI(v). States bound within the adiabatic approximation and having significant Franck-Condon overlap with IHI⁻ are shown with solid line. The dotted line indicates a shape resonance state.

find the halogen-atom wave functions $\Delta_h(R)$ supported by each adiabatic curve $U_k(R)$ and calculate their overlap with the anion ground state. A few of the adiabatic curves have a global minimum, and could support discrete states. However, most of the adiabatic curves contain only local minima or are purely repulsive. These curves should give rise to a continuous eigenvalue spectrum. Rather than treat some of the adiabatic curves differently from others, we use the DVR and a finite, one-dimensional harmonic-oscillator basis $P_i(R)$ to find the eigenvalues $\Delta_h(R)$ on each adiabatic curve. This means that, rather than the continuous eigenvalue spectrum expected at most energies, we get a series of discrete eigenvalues. The basis functions have a frequency of 200 cm⁻¹ and are centered at $(R_{\min} + R_{\max})/$ 2=3.90 Å for the IHI⁻ calculations. We use many basis functions, so the eigenvalues are closely spaced. This approach is quite similar in spirit to that of Bowman, who used an L^2 basis in his two-²¹ and three-dimensional studies²² of the photoelectron spectra of IHI⁻ and ClHCl⁻. Our approach is described in more detail elsewhere.⁴²

Recall that the intensities of the peaks in the photoelectron spectrum are given by Eq. (1), and the groundstate anion wave function Ψ_0^i is given by

$$\Psi_0^i(\rho,z,R) = \Xi_0^i(\rho,z)\Delta_0^i(R).$$
⁽²⁰⁾

 $\Xi_0^i(\rho,z)$ is the $\nu_2 = 0$, $\nu_3 = 0$ anion wave function obtained by solving Eq. (10) at a single value of R, and $\Delta_0^i(R)$ is the

In order to simulate the photoelectron spectrum, we

967

 $v_1 = 0$ anion wave function. We use separable potentials for the anion and assume the Q_1 normal mode is parallel to the scattering coordinate R. The wave function on the neutral potential is

$$\Psi_{k,h}^{f}(\rho,z,R) = \Xi_{k}^{f}(\rho,z;R)\Delta_{h}^{f}(R), \qquad (21)$$

where $\Delta_h^f(R)$ is the wave function with quantum number h obtained by solving the Schrödinger equation for halogen motion on the kth adiabatic curve. The wave functions can be written in terms of the two-dimensional harmonic-oscillator basis functions $X_{m,n}(\rho,z)$ and one-dimensional harmonic-oscillator basis functions $P_i(R)$,

$$\Xi_0^i(\rho,z) = \sum_{m',n'} c^i_{m',n',\sigma} X_{m',n'}(\rho,z)$$
(22)

and

$$\Delta_0^i(R) = \sum_{j'=1}^{N_R} d_{j',o}^i P_{j'}(R), \qquad (23)$$

and for the neutral,

$$\Xi_{k}^{f}(\rho, z; R) = \sum_{m,n} c_{m,n,k}^{f}(R) X_{m,n}(\rho, z)$$
(24)

and

$$\Delta_{h}^{f}(R) = \sum_{j=1}^{N_{R}} d_{j,h}^{f} P_{j}(R).$$
(25)

The same basis set is used for the anion and neutral. The intensity is then given by

$$I \propto |\langle \Psi^{i} | \Psi^{f} \rangle|^{2}$$

$$\propto \left| \int dR \int d\rho \int dz \Psi_{0}^{i}(\rho, z, R) \Psi_{k,h}^{f}(\rho, z, R) \right|^{2}$$

$$\propto \left| \int dR \Delta_{0}^{i}(R) \Delta_{h}^{f}(R) \int d\rho \int dz$$

$$\times \sum_{m',n'} c_{m',n',\sigma}^{i} X_{m',n'}(\rho, z) \sum_{m',n'} c_{m,n,k}^{f}(R) X_{m,n}(\rho, z) \right|^{2}.$$
(26)

As we are using the same orthonormal basis set,

$$\int d\rho \int dz X_{m',n'}(\rho,z) X_{m,n}(\rho,z) = \delta_{m',m} \delta_{n',n}, \quad (27)$$

for the anion and neutral we have

$$I \propto \left| \int dR \,\Delta_0^i(R) \Delta_h^f(R) \sum_{m,n} c_{m,n,o}^i c_{m,n,k}^f(R) \right|^2. \quad (28)$$

The integral over R is done by quadrature using 400 points in R and interpolating $c_{m,n,k}^f(R)$, since the coefficients change slowly with R within the adiabatic approximation. Note that the hydrogen wave function need not be explicitly calculated to determine the overlaps.

Because of the L^2 method used to calculate the wave functions $\Delta_h(R)$, this procedure yields a stick spectrum rather than a spectrum with peaks of various widths. This stick spectrum is then convoluted with a resolution function (for example, the instrumental resolution) to give a continuous spectrum. Using a basis set of $N_R = 90$ basis functions in R gives eigenvalues spaced by ≤ 10 meV. As the experimental resolution is slightly better than this, the following approach is used to improve the simulated spectrum. Eigenvalues and corresponding overlaps are determined using $N_R = 90$, 80, 70, 60 and the stick spectra are added. For repulsive ("direct scattering" states) changing the size of the basis will change the eigenvalues (see Ref. 42). Thus, a 2500–5000 line stick spectrum is obtained with the sticks spaced by ≤ 2 meV, which is then convoluted with the experimental resolution function (~8 meV resolution) to obtain a smooth spectrum. We have applied the adiabatic three-dimensional method to the photoelectron spectra of IHI⁻, IDI⁻, BrHBr⁻, BrDBr⁻, and BrHI⁻. These systems will be discussed in the next section.

III. RESULTS

A. IHI⁻ simulations using the LEPS-A potential

The I + HI reaction is the prototypical heavy + lightheavy reaction. Thus, there has been a great deal of theoretical work on this reaction which has predicted a number of interesting properties: oscillating reactivity as a function of reactant kinetic energy,^{24(c)} long-lived resonance states,^{9,10,14} and a bound state on a minimum-free-model potential-energy surface.^{25,26,46} New theoretical methods for treating heavy+light-heavy reactions are often tested on the I + HI reaction, usually employing the semiempirical LEPS-A potential.¹⁰ This surface has a collinear minimum-energy path and a barrier of 0.048 eV. Although recent experimental results^{4,6} have shown that the surface has some significant deficiencies, it has been used in nearly every theoretical treatment of the I + HI reaction, including simulations of the IHI⁻ photoelectron spectrum. It is therefore reasonable to test our three-dimensional adiabatic simulations on the LEPS-A surface so that our results can be compared to Schatz's exact simulations^{13,15} on this surface (and to the experimental spectra, as well).

Before presenting the three-dimensional adiabatic simulations, it is useful to compare the adiabatic curves obtained in collinear and three-dimensional adiabatic treatments. At large interiodine distance, collinear adiabatic curves correlate to I + HI(v), while three-dimensional adiabatic curves correlate to I + HI(v, j). A collinear simulation of the IHI⁻ photoelectron spectrum therefore requires the inclusion of only three adiabatic curves of gerade symmetry, corresponding to I + HI(v=0, 1, 2), while a three-dimensional simulation requires the consideration of about 60 states of σ_g symmetry, correlating to I + HI(v =0, j=0-27; v=1, j=0-20; v=2, j=0-10). Collinear adiabatic curves⁴⁷ for the I + HI reaction are shown in Fig. 3(b). The three curves are labeled by the antisymmetric stretch quantum number of the IHI complex. Adiabatic curves with $v_1 = 2n$ correlate to I + HI(v=n). The three adiabatic curves in a collinear calculation have no avoided crossings, hence the couplings between the adiabatic curves are always small-this explains the success of the adiabatic method in collinear calculations on this system. These small couplings can be approximately included using the

J. Chem. Phys., Vol. 97, No. 2, 15 July 1992

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FIG. 4. Threshold photodetachment (\cdots) and collinear simulated (--) photoelectron spectra of IHI⁻. The collinear simulation has been obtained using the LEPS-A potential, with zero-point bend, and has been shifted to lower EKE by 80 meV and convoluted with 5 meV Gaussians.

DIVAH (diagonally corrected vibrational adiabatic hypespherical) correction.¹¹

All three curves support states that are bound within the adiabatic approximation, several of which are shown by solid lines in Fig. 3(b). The $v_3 = 0$ adiabatic curve supports two bound states of IHI (with $v_1 = 0$ and 1), and a shape resonance indicated with a dotted line. The states indicated on the higher-lying adiabatic curves are Feshbach resonance states that can decay by coupling to lowerlying adiabatic curves. This coupling is ignored in the adiabatic calculation. These resonance states are responsible for the sharp peaks in simulations of the IHI⁻ photoelectron spectrum.

The simulated collinear photoelectron spectrum of IHI⁻ is shown in Fig. 4. The simulation uses a resolution of 5 meV so that the resonance peaks are clearly resolved. At this resolution, it is indistinguishable from the exact two-dimensional quantum scattering result.⁷ However, while the collinear simulation predicts the positions and intensities of the resonance states in the photoelectron spectrum of IHI⁻ with reasonable accuracy, it does not yield the "rotational threshold" features associated with the $v_3 = 0$ peak seen in the exact three-dimensional simulation¹⁴ as well as in the experimental spectrum (Fig. 1). This significant failure of the collinear approach prompted our interest in the adiabatic three-dimensional approach.

We now consider the three-dimensional adiabatic curves for the I + HI reaction which were derived in Sec. II [see Fig. 3(a)]. Some curves have wells, while many, especially at lower energy, are purely repulsive. Just as in the collinear simulation, the curves with wells should lead to sharp resonance features in the three-dimensional adiabatic simulation. As will be seen below, transitions to the closely spaced repulsive adiabatic curves which correlate to I + HI(v=0, j) give rise to the broad rotational threshold features seen in the experimental spectrum, but not reproduced in the collinear simulation.

In contrast to the collinear curves, the adiabatic curves

in three dimensions have numerous avoided crossings, especially at higher energy. The reason for this is that hydrogen antisymmetric stretch vibrations have a frequency of some 700 cm^{-1} , while (iodine) symmetric stretch motion occurs with a 100 cm^{-1} frequency. The separation of time scales is quite distinct. However, in three dimensions, we also have to consider the I-H-I bend, which becomes a hindered rotation at larger R_{II} , and finally a free HI rotation at the asymptotes. The HI(v=0) rotational constant is 6.4 cm^{-1,48} so, for low rotational levels, rotations occur more slowly than iodine-atom motion, violating the separation of time scales assumed in the adiabatic treatment. This causes the large number of avoided crossings in the adiabatic curves. Because of these, the adiabatic approach may not accurately predict scattering results such as reaction rates and product-state distributions. However, the adiabatic simulation of the IHI⁻ photoelectron spectrum should give accurate results when photodetachment occurs to curves with few avoided crossings in the Franck-Condon region. Also, the adiabatic approach is expected to be better for high-rotor states of the complex, as these involve faster hydrogen motion. Note that the twodimensional adiabatic surfaces derived by Grayce and Skodje²⁹ have far fewer crossings than the adiabatic curves in Fig. 3(a).

The experimental threshold photodetachment spectrum of IHI⁻ is shown in Fig. 5(a) and compared to Schatz's exact scattering simulation¹³ on the LEPS-A surface [Fig. 5(b)] and our adiabatic three-dimensional simulation [Fig. 5(c)]. The calculated spectra have been shifted to lower electron kinetic energy (eKE) by 80 meV and convoluted with 5 meV Gaussians to facilitate comparison with experiment. The neutral scattering energy (SE) (measured relative to the bottom of the well for the lowest-energy diatomic fragment) and the electron kinetic energy in the photoelectron spectrum are, in general, related by

$$SE = A - eKE$$
(29)

with

$$A = h\nu + ZPE(HY) - D_0(XHY^-) - EA(X),$$

where hv is the photon energy of the detachment laser (4.660 eV for IHI⁻ and IDI⁻, and 5.825 eV for BrHI⁻, BrHBr⁻, and BrDBr⁻), ZPE is the zero-point energy of the HY diatomic fragment,⁴⁸ $D_0(XHY^-)$ is the dissociation energy of XHY⁻,⁴⁹ to X⁻ +HY, and EA(X) is the electron affinity of the remaining atom.⁵⁰ The uncertainty in the conversion factor A is 0.05 eV for BrHI⁻ and BrH(D)Br⁻ and 0.13 eV for IH(D)I⁻, and is due almost entirely to the uncertainty in $D_0(XHY^-)$.⁴⁹ Note that states with *lowest* internal energy occur at the *highest* electron kinetic energy. The two simulated spectra are quite similar and the features in the two simulations will now be compared in detail.

The lowest adiabatic curve in Fig. 3(a) has a well at $R_{II} = 3.63$ Å, which supports a state of the IHI complex that lies below I + HI(v=0, j=0). This is a "vibrationally bound" state of IHI [peak A, Fig. 5(c)]; the reasons for the existence of this state on the minimum-free LEPS-A po-



FIG. 5. Experimental and simulated photoelectron spectra of IHI^- . (a) Experimental threshold photodetachment spectrum of IHI^- (—). (b) Simulated photoelectron spectrum of IHI^- of Schatz, calculated using the exact 3D CCH scattering method and the LEPS-A potential. (c) Simulated photoelectron spectrum of IHI^- calculated using the adiabatic 3D method and the LEPS-A potential. The simulated spectra have been convoluted with a uniform resolution of 5 meV and shifted to lower electron kinetic energy by 80 meV to facilitate comparison with experiment.

tential have been discussed in detail elsewhere.^{25,26,46} This state is predicted to lie at a scattering energy of 0.137 eV in our adiabatic calculation. This is the same energy as was found in the full quantum calculations of Clary and Connor⁴⁶ and the L^2 calculation of Gazdy and Bowman²² (this is a bound state and therefore does not appear in Schatz's scattering calculation). This state is centered at $R_{II} = 3.63$ Å, while the IHI⁻ anion has been assumed to have $R_{II} = 3.88$ Å, so there is little Franck-Condon overlap with the bound state—it has only 3% the intensity of the large peak at 0.158 eV [peak C, Fig. 5(c)].

The $v_3 = 0$ adiabatic curves also support long-lived resonance states which, in contrast to the "vibrationally bound" state, lie above I + HI(v=0, j=0). The adiabatic simulation has a sharp peak at 0.148 eV [peak B, Fig. 5(c)] corresponding to a state with one quantum of symmetric stretch excitation. This (100) resonance was found at 0.149 eV in the CCH calculations, but has very low intensity, so it is not obvious in Fig. 5(b). The intense peak at 0.158 eV [peak C, Fig. 5(c)] is at the energy of the intense (200) resonance in the CCH calculations [0.159 eV, peak C, Fig. 5(b)]. Thus the adiabatic method accurately predicts the bound and resonance states with $v_3 = 0$.

In addition to resonance states of the [IHI] complex, the adiabatic simulation yields a series of broad peaks between 0.18 and 0.33 eV scattering energy. These appear to be the "rotational threshold" peaks which appear both in Schatz's simulation and the experimental IHI⁻ threshold photodetachment spectrum. The origin of these peaks is evident from the adiabatic curves in Fig. 3(a). There is a series of adiabatic curves correlating to I+HI(v=0, j=4-14) which are nearly flat in the Franck-Condon region [Fig. 3(a)]. In the Franck-Condon region, the spacings between these curves are similar to the spacing of the asymptotic HI rotational levels to which they correlate, and in the adiabatic simulation, one expects a series of broad peaks with this same energy interval from transitions to this series of curves. This is exactly what is seen in the simulated $v_3 = 0$ feature in Fig. 5(c). The similarity of the peak spacings to the asymptotic HI rotational spacings suggests that the peaks are from transitions to nearly free internal rotor states of the IHI complex; this is supported by the pictures of the H-atom wave functions associated with these adiabatic curves which were obtained by Kubach.27

The adiabatic calculations show an intensity profile that varies smoothly with the rotational level, while the exact simulations show a nonmonotonic dependence. This variation in intensity may be due to couplings between the adiabatic curves at short R, where there are some avoided crossings, or to coupling between close-lying adiabatic curves at large R. Our adiabatic calculation ignores these couplings.

The agreement between the adiabatic and exact simulations is not as good for the resonances in the $v_3 = 2$ manifold. We find resonance peaks at 0.333, 0.344, 0.354, and 0.365 eV [the series of peaks labeled *D* in Fig. 5(c)], while resonances in the exact calculation appear at 0.340, 0.353, 0.368, and 0.380 eV [the series of peaks labeled *D* in Fig. 5(b)]. The somewhat worse agreement for the $v_3 = 2$ resonances than the $v_3 = 0$ states is likely due to the number of avoided crossings in the Franck-Condon region for these curves [Fig. 3(a)]; these are not treated accurately in our adiabatic approximation. Both simulations predict that the rotational threshold contribution will be much smaller for the $v_3 = 2$ peak, where the photoelectron spectrum is dominated by overlap with resonance states.

There is only one resonance in the $v_3 = 4$ manifold that has good Franck-Condon overlap with the anion. This is the (004) resonance, which we find at 0.562 eV [peak *F*, Fig. 5(c)]. Schatz's calculation did not extend to this energy range, but the analogous peak appears at 0.574 eV in Bowman's three-dimensional L^2 calculation.²² In summary, results of simulations of the IHI⁻ photoelectron spectrum on the LEPS-A potential show that the adiabatic three-dimensional approach accurately reproduces the $v_3 = 0$ bound state and resonances seen in full three-dimensional calculations and does a much better job of reproducing the direct scattering features (the rotational thresholds) of the photoelectron spectrum than do collinear calculations. The adiabatic method only does a fair job of reproducing the $v_3 = 2$ resonances, because of the number of avoided crossings in this region. The efficiency of the method allows us to apply it to a variety of systems for which scattering calculations have not been carried out, or have been carried out over a limited energy range.

B. IDI-: LEPS-A surface

As the major progression in the IHI⁻ photoelectron spectrum is due the hydrogen antisymmetric stretch, there is a large isotope shift upon deuteration. The IDI⁻ photoelectron spectrum^{4,51} therefore provides additional information on the potential-energy surface for the reaction. In addition, Schatz has performed an "exact" simulation of the IDI⁻ photoelectron spectrum.¹⁷ However, the theoretical treatment of the photoelectron spectrum of deuterides is more computationally demanding than hydrides as the density of rovibrational states for deuteride systems is roughly twice that of hydride systems. Due to the difficulty of the scattering calculation, the low-energy portion of the simulated spectrum is converged, but the convergence of the high-energy region is less certain. We have simulated the photoelectron spectrum of IDI⁻ on the LEPS-A potential using the adiabatic approach, obtaining converged (but approximate) results over a wider energy range than was considered by Schatz.

The experimental photoelectron⁴ and high-resolution photodetachment⁵¹ spectra of IDI are shown in Fig. 6(a). As in Fig. 5(a), the peaks are labeled by the v_3 (antisymmetric stretch) quantum number of the neutral complex. As can be seen, the high-resolution IDI- spectrum looks quite different from the IHI- spectrum [Fig. 5(a)]. In IDI⁻, the $v_3 = 0$ peak does not show the discrete "rotational threshold" features seen in IHI⁻ at comparable resolution. The experimental photodetachment spectrum also shows two features labeled $v_3 = 2$ and 2' spaced by about 0.035 eV. This is much larger than the $\sim 0.010-$ 0.015 eV spacing one would expect between resonance states, so the nature of these two features is not clear at first glance. As in IHI⁻, peaks narrow to higher v_3 , finally resulting in a $v_3 = 4$ peak which is 60 cm⁻¹ wide; this peak is likely due to a resonance.

Simulations of the photoelectron spectrum of IDI⁻ have been carried out to help understand some of the features observed in the experimental spectrum, such as the absence of resolved rotational threshold features in the $v_3 = 0$ peak and the presence of peak $v_3 = 2'$. First, we will compare our adiabatic three-dimensional simulation to Schatz's simulation, then we will compare the simulated spectra to experiment to gain information on deficiencies in the LEPS-A potential for the I + HI reaction.



FIG. 6. (a) Experimental photoelectron spectrum of IDI^- obtained using the fixed-frequency photoelectron spectrometer (---), and higherresolution threshold photodetachment spectrum (--). The peak heights in the threshold spectra have been scaled to those obtained using the fixed-frequency spectrometer and the peaks have been shifted by 14 meV. (b) Simulated photoelectron spectrum of IDI^- of Schatz, calculated using the exact 3D CCH scattering method and the LEPS-A potential. Peak *C* has been clipped at 12% of its true intensity. (c) Simulated photoelectron spectrum of IDI^- calculated using the adiabatic 3D method and the LEPS-A potential. The simulated spectra have been convoluted with a uniform resolution of 5 meV and shifted to lower electron kinetic energy by 80 meV to facilitate comparison with experiment.

adiabatic threesimulation and our Schatz's dimensional simulation are shown in Figs. 6(b) and 6(c), respectively. The simulated spectra have been shifted 80 meV to lower electron kinetic energy and convoluted with 5 meV Gaussians to facilitate comparison with experiment. The adiabatic results are in better agreement with the exact scattering results at low scattering energy than at high scattering energy. Peak A, which is due to a resonance transition to the quasibound (100) level of IDI, occurs at 0.121 eV in Fig. 6(b) and at 0.123 eV in Fig. 6(c). [Schatz's calculation of the I + DI reaction probability¹⁷ shows a resonance due to the IDI (000) level, but this state has negligible Franck-Condon overlap with the anion.]



FIG. 7. Three-dimensional adiabatic curves of σ_g symmetry for the I + DI system on the LEPS-A potential. Each curve correlates to I + DI(v, j).

The $v_3 = 2$ features consist of several resonances in the 0.24-0.29 eV energy range in both the adiabatic and exact calculations [peaks *B*, Fig. 6(b) and 6(c)]. The $v_3 = 4$ feature, which consists of a single resonance in the collinear simulation,⁴ is composed of three intense resonances (at 0.378, 0.392, and 0.404 eV) in the exact calculation [peaks *D*, Fig. 6(b)]. In the adiabatic calculation, we find two sharp $v_3 = 4$ resonance peaks at 0.393 and 0.399 eV [peaks *D*, Fig. 6(c)]. Resonance positions in the adiabatic simulation are in good agreement with the full scattering calculations for the $v_3 = 0$ and 2 features. It is difficult to determine if discrepancies in the $v_3 = 4$ features are due to failure of the adiabatic approximation or to lack of convergence of the full three-dimensional scattering calculation at this high energy.

In addition to the resonance features, both simulations of the photoelectron spectrum of IDI⁻ also predict a number of features due to direct scattering. Both simulations of the $v_3 = 0$ peak show rotational threshold features to the high scattering energy side of peak A, although they are not as well separated as in the IHI⁻ simulation, an expected result due to the smaller spacings between the IDI hindered rotor levels responsible for these features. This is consistent with the experimental finding of resolved threshold features with a width of ~20 meV separated by 20–25 meV in IHI⁻ [Fig. 5(a)], while the IDI⁻ photoelectron spectrum [Fig. 6(a)] shows no resolved features in the $v_3 = 0$ peak, at the same experimental resolution.⁵¹

Schatz's simulation is dominated by the broad peak at 0.33 eV [peak C, Fig. 6(b)]. A much smaller version of this peak appears at 0.32 eV in the adiabatic simulation [peak C, Fig. 6(c)] and a similar feature also appears in the adiabatic IHI⁻ simulation [peak E, Fig. 5(c)] though it has lower intensity than in IDI⁻. The origin of this feature becomes clear if one looks at the I + DI adiabatic curves shown in Fig. 7. Peak C appears just above the I + DI(v = 1) threshold. Figure 7 shows there is a large number of closely spaced adiabatic curves in this energy range which correlate to I + DI (v=1, low j). Peak C thus appears to be due to overlapping transitions to these repulsive adiabatic curves. The reason for the very different peak C intensities in Figs. 6(b) and 6(c) may be because Schatz's

calculation is not well converged at this high energy.

While the adiabatic picture offers a clear picture of the origin of peak C in the IDI⁻ simulations, what is more interesting is that this peak probably corresponds to the aforementioned $v_3 = 2'$ peak in the *experimental* IDI⁻ photodetachment spectrum. The experimental and simulated peaks occur at roughly the same energy, and the energy discrepancy is even smaller on the LEPS-C I + HI potential-energy surface discussed below.

More generally, comparing the simulated and experimental photoelectron spectra of IHI⁻ and IDI⁻ allows us to point out some deficiencies in the LEPS-A potential. The LEPS-A potential supports a bound state of IHI and several long-lived $v_3 = 0$ resonance states of IHI and IDI. Transitions to the resonances yield the intense peaks C and A in the IHI^- and IDI^- simulations, respectively, which are not observed in the experimental spectra. This implies that, on the true potential for the I + HI reaction, the $v_3 = 0$ adiabatic curves do not have wells and hence do not support resonances (or bound states). One way to eliminate these wells is to raise the barrier on the potentialenergy surface. A higher barrier would also shift the simulated spectrum to higher scattering energy, reducing the 80 meV offset needed to line up the experimental and LEPS-A simulations. This is a slightly less compelling reason to increase the barrier height, since this 80 meV shift is less than the 130 meV uncertainty⁴⁹ in the heat of formation of IHI⁻.

In addition, the simulated spectra have too much Franck-Condon intensity in the $v_3 = 0$ peak and not enough in the $v_3 = 2$ peak, and the v_3 peaks are spaced too far apart in the LEPS-A simulations, a feature we have also seen with a LEPS potential for the Br + HBr reaction. While the potential used for IHI⁻ does affect the intensity distribution, most of the differences between experiment and the simulations are likely due to discrepancies in the LEPS-A potential, and raising the barrier on the LEPS-A potential is a good first step in alleviating these discrepancies. We note that the LEPS-A surface was constructed in the absence of any experimental data on the I + HI reaction, so it is not surprising that substantial modification is required.

C. IHI-: LEPS-C surface

Recently, Schatz has simulated the low-energy portion of the photoelectron spectrum of IHI⁻ in three dimensions on a series of LEPS surfaces with barriers of 0.048 eV (LEPS-A) to 0.243 eV (LEPS-D).¹⁶ He found that the LEPS-C surface, with a 0.161 eV barrier, leads to a simulated spectrum in somewhat better agreement with the experimental results than the LEPS-A surface. In particular, the LEPS-C surface supports no bound or long-lived resonance states in the $v_3 = 0$ manifold—all the observed features are due to rotational thresholds. Also, due to the higher barrier on the LEPS-C surface, only a 40 meV shift is required to align the simulated and experimental spectra, using the known thermodynamics of the IHI⁻/I+HI system, compared to 80 meV for the LEPS-A surface. As Schatz's simulation only covers the $v_3 = 0$ peak, we have



FIG. 8. Three-dimensional adiabatic curves of σ_g symmetry for the I + HI system on the LEPS-C potential. Each curve correlates to I + HI(v, j).

calculated the photoelectron spectrum of IHI⁻ on the LEPS-C surface using the adiabatic approach over the entire energy range observed in the experiment.

Adiabatic curves for the I + HI reaction on the LEPS-C potential are shown in Fig. 8. The lowest adiabatic curves are purely repulsive, so the LEPS-C potential does not support a bound state or $v_3 = 0$ resonance state of IHI. This is in contrast to the LEPS-A potential, where the lowest adiabatic curve has a well that supports a bound state, and higher-lying adiabatic curves support $v_3 = 0$ resonance states.

The adiabatic simulation of the IHI⁻ photoelectron spectrum using the LEPS-C potential (at 5 meV resolution) is shown in Fig. 9, along with the high-resolution threshold photodetachment spectrum. The simulated v_3 = 0 peak consists of a series of rotational thresholds dominated by peak A at 0.22 eV. This peak is not due to a resonance, as the lowest adiabatic curves on the LEPS-C potential are purely repulsive. The adiabatic results show a series of $v_3 = 2$ resonance peaks at 0.404, 0.416, and 0.425 eV (peaks *B-D*, Fig. 9) and a sharp $v_3 = 4$ resonance at



FIG. 9. Threshold photodetachment (\cdots) and simulated (-) photoelectron spectra of IHI⁻ on the LEPS-C potential. The simulation is obtained using the adiabatic 3D method and has been shifted 40 meV to lower eKE and convoluted with a uniform 5 meV resolution.



FIG. 10. Threshold photodetachment (\cdots) and simulated (-) photoelectron spectra of IDI⁻ on the LEPS-C potential. The simulation is obtained using the adiabatic 3D method and has been shifted 20 meV to lower eKE and convoluted at 5 meV resolution.

0.619 eV (peak E, Fig. 9). Note that, at 5 meV resolution, the resonance peaks are clearly narrower than the rotational threshold peaks. The presence of resonances with $v_3 = 2$ and 4 and absence of resonances with $v_3 = 0$ is in accord with the experimental observations. The LEPS-C simulation shows more intensity in the $v_3 = 2$ and 4 peaks than the LEPS-A simulation, in agreement with experiment.

The LEPS-C surface is certainly an improvement over the LEPS-A potential, although it still does not accurately reproduce the IHI⁻ photoelectron spectrum. The simulated $v_3 = 0$ manifold is dominated by a single peak, while the experimental spectrum consists of five peaks with similar intensity. Also, the $v_3 = 2$ to $v_3 = 4$ spacing is too large in the simulation, a common failure with LEPS potentials which is likely due to the repulsive walls of the LEPS surface being too steep.⁵ Merely changing the Sato parameter (and hence the barrier) on the LEPS surface may not give enough flexibility to accurately reproduce the experimental results. An alternate approach will be discussed in Sec. III F with respect to the BrHBr⁻ spectrum.

D. IDI-: LEPS-C potential

The simulated photoelectron spectrum of IDI^- on the LEPS-C potential obtained using the adiabatic threedimensional method is shown in Fig. 10 along with the threshold photodetachment results.⁵¹ The simulated spectrum is shown at 5 meV resolution and has been shifted 20 meV to lower electron kinetic energy. As with IHI⁻, the IDI⁻ simulation on the LEPS-C potential supports no $v_3 = 0$ resonance states, in accord with experiment (peak A, Fig. 10). The simulation of the $v_3 = 2$ feature consists of two series of peaks—a group of resonance peaks (feature B, Fig. 10, with the largest peak at 0.339 eV) and a peak due to overlap with states at the I + DI(v=1) threshold (feature C, Fig. 10, 0.372 eV). The adiabatic simulation of the IDI⁻ spectrum on the LEPS-A potential also shows these two $v_3 = 2$ features [features B and C, Fig. 6(c)], but

J. Chem. Phys., Vol. 97, No. 2, 15 July 1992

the spacing between the resonance and threshold features is smaller on the LEPS-C surface. These two features appear in the experimental spectrum [peaks 2 and 2' in Fig. 6(a)], and the simulation suggests that, in the experimental spectrum, feature 2 is due to $v_3 = 2$ resonance states and feature 2' is due to states at the I + DI(v=1) threshold (as was discussed in Sec. III B). The spacing between these features is sensitive to how repulsive the potential-energy surface for the I + DI reaction is near the barrier, with a more repulsive surface (such as the LEPS-C potential) leading to a smaller *B*-*C* spacing. The LEPS-C potential supports a single $v_3 = 4$ resonance, at 0.459 eV. The agreement between the experimental and simulated $v_3 = 2$ and 4 features is surprisingly good.

E. BrHI-: BP LEPS surface

In an earlier study of the BrHI⁻ photoelectron spectrum,⁶ we found that collinear simulations on the Broida-Persky (BP) LEPS surface⁵² successfully reproduced peak positions and intensities seen experimentally, but the simulated peaks were much narrower than those observed experimentally. An adiabatic three-dimensional simulation should show whether this discrepancy in peak widths is due to the collinear simulation or deficiencies in the BP surface. While the LEPS-A surface for the I + HI reaction was constructed without the benefit of experimental results, the Br + HI reaction is easier to study experimentally and the BP LEPS surface was constructed to reproduce experimental rate constants for the Br + HI reaction at several temperatures, as well as the product HBr (v=2)/(v=1) ratio at 300 K in classical trajectory calculations. The BP surface matches the Br + HI exothermicity (0.704 eV) and has a collinear minimum energy path with a 0.009 eV barrier. While the neutral potential for Br + HIis better characterized than the I + HI potential, even less is known about BrHI⁻ than about IHI⁻. An earlier collinear study of the BrHI⁻ photoelectron spectrum⁸ used physically reasonable values for the anion frequencies and geometry-we will use the same values in this study. The parameters are summarized in Table I.

Neither full nor approximate three-dimensional calculations of the BrHI⁻ photoelectron spectrum have been carried out previously. The difficulty in these calculations lies in the large number of distinguishable products that can be produced. The collinear calculations predict that the photoelectron experiment accesses levels correlating to I + HBr(v=0,1,2,3) and Br + HI(v=0,1). This is in contrast to the three product vibrational states accessed in IHI⁻ photodetachment. Unlike the other systems we have discussed, the Br + HI system is not symmetrical. Thus, the same level of convergence for Br + HI as for I + HIwould require a basis set of about twice the size, raising the computation time by a factor of 8. This is rather prohibitive, so a moderate basis of 1404 basis functions with N_r = 18 and N_z = 78 was used to calculate the lowest 100 hydrogenic states. This required twice the execution time as for IHI⁻. Levels correlating to I + HBr(v=0,1) are well converged and to I + HBr(v=2) and



FIG. 11. Experimental (—) and simulated (…) photoelectron spectra of BrHI⁻. The simulation has been obtained using the adiabatic 3D method and the BP LEPS potential and has been shifted by 62 meV to lower electron kinetic energy and convoluted with the instrumental resolution function. The three peaks at eKE<1.25 eV in the experimental spectrum are from transitions to an excited electronic state of the BrHI complex (see Ref. 8). The instrumental resolution is 12 meV at 0.85 eV eKE ($v_3 = 0$) and improves to 7 meV at 0.55 eV eKE ($v_3 = 4$), the actual function is given in Ref. 5.

Br +HI(v=0) are fairly well converged. This covers the major features observed experimentally.

The simulated photoelectron spectrum of BrHI⁻ at the resolution of the fixed-frequency photoelectron spectrometer is shown in Fig. 11. The simulation consists of two broad, intense peaks at 0.336 eV ($v_3 = 0$) and 0.632 eV $(v_3 = 1)$ due to overlap to states correlating to I + HBr(v=0) and I + HBr(v=1), respectively, and a slightly smaller $v_3 = 3$ peak at 0.903 eV which corresponds to I + HBr(v=2). While the collinear calculation predicts a very small $v_3 = 2$ resonance peak due to Br + HI(v=0) just below the I + HBr peak, this feature is too weak to be positively identified in Fig. 11. At moderate resolution (the resolution available in the fixed-frequency photoelectron experiment), the broad features are expected to show barely resolved structure due to rotational thresholds. The positions of the peaks in the present study are in good agreement with those found in our earlier, collinear study.⁸ In both cases, a shift of 62 meV is required to align the experimental and simulated spectra. This is at the level of the uncertainty in the dissociation energy of BrHI^{-,49} which is used to determine the conversion from scattering energy to electron kinetic energy.

The peaks in the three-dimensional adiabatic simulation have similar intensities to those found in the collinear simulation. The most striking difference between the collinear and adiabatic 3D results is in the peak widths: the $v_3 = 0$, 1, 3 peaks have widths of 100, 85, and 62 meV, respectively in the present study and widths of 43, 36, and 15 meV in the collinear study.⁸ The widths of these peaks in the 3D adiabatic simulations are due to overlapping rotational thresholds. This resolves some of the discrepancy between the calculated and experimental widths. All three experimental peaks have widths of 160–170 meV and lack resolved rotational threshold features (the resolution of the 213 nm photoelectron spectrum is ~ 30 meV in this energy range, but spectra taken at 266 nm show a similar lack of structure at 8 meV resolution).

The discrepancies between the three-dimensional adiabatic simulation and the experimental results could be due to errors in the BrHI⁻ potential, which is not well known. It could, however, point out deficiencies in the BP surface, as it has been found for BrHBr⁻ that collinear simulations on a LEPS surface give peaks that are much too narrow.⁵ The Br + HI reaction could also proceed via a noncollinear minimum energy path, while the minimum-energy path on the BP surface is collinear. Alternatively, it has been pointed out⁸ that photodetachment of BrHI⁻ could access two low-lying excited electronic states of the neutral complex, in addition to the ground state. Transitions to one of these excited states, which correlates to $I^*({}^2P_{1/2})$ + HBr, are clearly observed in the photoelectron spectrum below 1.2 eV eKE and obscure any structure due to transitions correlating to I + HBr(v=3) and Br + HI(v=1) on the ground electronic surface. The other low-lying excited electronic state is due to the splitting caused by the interaction of the open-shelled iodine atom with the HBr dipole. Transitions to this state are expected to lie in the same energy range as the ground-state features and therefore could cause the observed peaks to broaden. The observed discrepancies between the simulated and experimental photoelectron spectra of BrHI- are likely due to a combination of these effects.

F. BrHBr⁻ on a fitted surface

In an earlier paper,⁵ the photoelectron spectrum of $BrHBr^-$ was fit using an empirical "effective" collinear potential-energy surface for the Br + HBr reaction. We would like to test this fit by simulating the photoelectron spectrum in three dimensions using the fitted potential. This requires a full three-dimensional surface, so the first step is to extend the collinear surface to three dimensions.

The three-dimensional Br + HBr surface is constructed by combining information from a fitted collinear and a reference LEPS potential. The fitted potential is completely empirical, and its functional form is given in Ref. 5. For the reference potential, we use the LEPS potential used in our earlier study of the Br + HBr reaction.^{5,53} It has the same collinear barrier and saddle-point position as the fitted collinear surface. However, as was shown in the earlier paper, simulations using this LEPS surface do not accurately reproduce the experimental spectrum. To distinguish between quantities calculated using collinear and noncollinear geometries we define

$$\Delta = (R_{\rm HBr} + R_{\rm BrH}) - R_{\rm BrBr}, \qquad (30)$$

so that $\Delta = 0$ at collinear geometries and $\Delta > 0$ at noncollinear geometries.

The fitted surface in Ref. 5 is an "effective" collinear surface because it implicitly includes the zero-point bend energy at every point. The first step is to approximately remove this energy to form a true collinear surface

TABLE II. Parameters for the Br+HBr potential.^a

R _{Br-Br} (Å)	<i>x</i> 1 (Å)	b (kJ/mol)	h (kJ/mol)	k (kJ/mol/Ų)	q (kJ/mol/Å ⁴)
5.2	1.676	-377.5	360.0	1220	100.0
5.7	2.030	-377.65	370.0	1180	50.0
6.2	2.3835	-377.8	376.0	1150	20.0
7.0	2.949	-378.0	377.0	1130	5.0
8.0	3.656	378.15	377.8	1130	3.0
9.0	4.363	-378.25	378.0	1130	2.0
10.0	5.070	-378.28	378.1	1130	1.0
11.0	5.778	-378.3	378.2	1130	0.5
12.0	6.485	-378.31	378.3	1130	0.2

^aParameters for $R_{\text{Br-Br}} < 5.2$ Å and the form of the potential are given in Ref. 5. Note that k and q should be in units of 10³ kJ/mol/Å² and 10³ kJ/mol/Å⁴, respectively, in Ref. 5.

$V_{\rm col}(r_{\rm HBr}, r_{\rm BrH}, \Delta = 0)$

$$= V_{\text{fit}}(r_{\text{HBr}}, r_{\text{BrH}}, \Delta = 0) - \text{ZPE}(r_{\text{HBr}}, r_{\text{BrH}}, \Delta = 0). \quad (31)$$

The zero-point bend energy is calculated on the reference LEPS potential at each collinear geometry, within the harmonic approximation, as described by Bowman.⁵⁴ For the zero-point-energy calculation *only*, a mass of 1.5 amu is used for the hydrogen atom. This is so the resulting three-dimensional potential-energy surfaces will be the same for Br + HBr and Br + DBr. The resulting collinear surface has a barrier height of 0.44 eV.

At collinear geometries, the difference between the reference LEPS potential and the fitted collinear surface is

$$\Delta V(r_{\rm HBr}, r_{\rm BrH}, \Delta = 0)$$

= $V_{\rm col}(r_{\rm HBr}, r_{\rm BrH}, \Delta = 0) - V_{\rm LEPS}(r_{\rm HBr}, r_{\rm BrH}, \Delta = 0).$ (32)

The global fitted potential is then defined as

 $V_{3 \text{ Dfit}}(r_{\text{HBr}}, r_{\text{BrH}}, \Delta)$

$$= V_{\text{LEPS}}(r_{\text{HBr}}, r_{\text{BrH}}, \Delta) + \Delta V(r_{\text{HBr}}, r_{\text{BrH}}, \Delta = 0). \quad (33)$$

In our collinear work,⁵ the fitted potential $V_{\rm fit}$ was constructed over the range 2.6 $\leq R_{\rm HBr} + R_{\rm BrH} \leq 4.7$ Å. However, in three dimensions, a geometry such as H-Br-Br with $R_{\rm BrH} = 1.4$ Å, $R_{\rm HBr} = 4.9$ Å, $R_{\rm BrBr} = 3.5$ Å, and $R_{\rm HBr} + R_{\rm BrH} = 6.3$ Å can be reached at reasonable energies. This is outside the range where $V_{\rm fit}$ is defined, so we extend the fitted potential to the range 2.6 $\leq R_{\rm HBr} + R_{\rm BrH} \leq 11.0$ Å. The new parameters for $R_{\rm HBr} + R_{\rm BrH} > 4.7$ Å were found by approximately matching the fitted potential to the reference LEPS potential at collinear geometries in this asymptotic region. The additional parameters for the fitted potential are given in Table II.

The experimental photoelectron spectrum of BrHBr⁻ is shown in Fig. 12 (solid line) and compared with the collinear simulation (dashed line) and the threedimensional adiabatic simulation (dotted line). As with the effective collinear calculation, the three-dimensional adiabatic simulation provides a reasonable fit to the experimental spectrum. The peak intensities and widths are well reproduced in the fitted spectrum (in fact, the noncollinear



FIG. 12. Experimental (-) and simulated photoelectron spectra of BrHBr⁻. Both a collinear (--) and adiabatic 3D (\cdots) simulation are shown. The experimental peaks at eKE < 0.8 eV have been assigned (Ref. 5) to an excited state of the BrHBr complex. Both simulations use the fitted potential and have been convoluted with the instrumental resolution function. Parameters used for the fitted potential are given in Table II.

simulation does a better job of reproducing the peak widths and shapes than the collinear simulation). Note that the peaks narrow as v_3 increases (to lower electron kinetic energy), finally giving a resonance peak for $v_3 = 4$. The experimental $v_3 = 4$ peak lies on top of the $v_3 = 0$ peak for transitions to an excited electronic state of the BrHBr complex, corresponding to the Br*(${}^2P_{1/2}$) + HBr reaction, thus it is difficult to compare the experimental and simulated intensities of this peak. Transitions to the excited electronic state were not considered in the present study.

The simulated BrHBr⁻ photoelectron spectrum does not show the resolved rotational threshold peaks found for IHI⁻.⁶ The reason for this can clearly be seen by comparing the adiabatic curves for Br + HBr (Fig. 13) and I + HI [Fig. 3(a)]. The $v_3 = 0$ Br + HBr curves are much more repulsive in the Franck-Condon region than the I + HI curves. Thus, each rotational threshold peak is so broad that it merges with neighboring peaks, resulting in a single broad feature. The adiabatic curves for Br + HBr are more repulsive because the minimum energy path for the Br + HBr reaction on the fitted surface is much steeper than on the LEPS-A or C surfaces used for the I+HI reaction.

It is interesting to compare the results of the adiabatic collinear simulation with those of the adiabatic threedimensional simulation. The overall peak intensities, positions of peaks corresponding to high v_3 levels, and peak widths are different in the two simulations. In the threedimensional simulation, the $v_3 = 0$ peak is noticeably less intense than in the collinear simulation. The positions of the $v_3 = 0$ and $v_3 = 2$ peaks are in good agreement with experiment, while the $v_3 = 4$ peak has shifted some 20 meV to lower electron kinetic energy from both the collinear simulation and experiment. Similar shifts in the positions of high antisymmetric stretch peaks in going from effective collinear to three-dimensional calculations have been also seen in the IHI⁻ system. This is probably because the



FIG. 13. Three-dimensional adiabatic curves of σ_g symmetry for the Br + HBr system on the fitted potential. Each curve correlates to Br + HBr(v, j).

effective bend potential seen by the $v_3 = 4$ wave function is somewhat steeper than that seen by the $v_3 = 0$ wave function. Unlike BrHI⁻, where peaks in the three-dimensional simulation are significantly broader than the collinear peaks, peaks in the three-dimensional BrHBr⁻ simulation are only slightly broader than the collinear ones.

G. BrDBr⁻ on the fitted surface

The photoelectron spectrum of BrDBr⁻ was simulated using the same potential-energy surface as for BrHBr⁻. The resulting collinear and adiabatic three-dimensional simulations are shown in Fig. 14 (dashed and dotted lines, respectively) and compared with experiment (solid line). Again, the simulated photoelectron spectra are in very good agreement with experiment. The peaks for BrDBr⁻ narrow as the v_3 quantum number increases, dropping from a width of > 140 meV for $v_3 = 0$ to 12 meV for v_3 = 6. The $v_3 = 6$ peak in the experimental spectrum lies on top of the $v_3 = 0$ peak for transitions to an excited electronic state of the [BrDBr] complex. Transitions to this excited state are not considered in this study. While BrDBr⁻ does give a sharp resonance peak, it is much less intense than the $v_3 = 4$ peak in BrHBr⁻.



FIG. 14. Same as Fig. 12, but for BrDBr⁻.

J. Chem. Phys., Vol. 97, No. 2, 15 July 1992

The BrHBr⁻ and BrDBr⁻ studies suggest that varying the bending potential will not significantly affect the simulations, assuming a linear anion and a reaction with a collinear minimum-energy path. This study shows a simple way to extend a collinear surface for a bimolecular reaction to three dimensions. This is very useful, since, while there exist several empirical functions for fitting a collinear potential surface, fitting a full three-dimensional potential is quite difficult. For collinearly dominated reactions, where the noncollinear portion of the potential need not be known as accurately as the collinear portion, an approximate three-dimensional surface can be constructed by fitting an empirical collinear surface to experimental results using collinear calculations and extending the surface to three dimensions as above. The surface can then be refined using three-dimensional calculations, or a combination of collinear and three-dimensional calculations. It would clearly be very useful to do an exact three-dimensional simulation of the BrHBr⁻ photoelectron spectrum on our new surface.

IV. CONCLUSIONS

We have simulated the photoelectron spectra of the bihalide anions XHY⁻ (X=Br, I) using a threedimensional adiabatic method which has been adapted from the work by Kubach.²⁷ This method provides an efficient means of simulating these spectra, and therefore holds considerable promise for developing improved potential-energy surfaces for the X + HY reactions considered in this study. The accuracy of this approach has been tested by comparing adiabatic simulations of the IHI⁻ and IDI⁻ photoelectron spectra with the exact (J = 0) scattering results of Schatz.^{15,17} Adiabatic simulations of the $v_3 = 0$ resonance peaks on the LEPS-A surface are in good agreement with the exact simulation, while the agreement in the $v_3 = 2$ peaks is not as good, presumably due to the number of avoided crossings that the corresponding adiabatic curves undergo in the Franck-Condon region. A notable improvement of this approach over earlier approximate simulation schemes is that it predicts the rotational threshold features associated with the $v_3 = 0$ peak that have been seen in the exact simulations and the experimental IHI⁻ threshold photodetachment spectrum. The adiabatic approach also provides a clear explanation of the origin of these features and the $v_3 = 2'$ peak seen in the threshold photodetachment spectrum of IDI-.

The adiabatic method has also been used to simulate the IHI⁻ and IDI⁻ spectra using the LEPS-C potential¹⁶ for the I + HI reaction. These simulations are in better agreement with experiment than simulations on the LEPS-A potential, implying that the I + HI surface has a larger barrier than on the LEPS-A potential and, consequently, that IHI does not support any vibrationally bound states. Simulations of the BrHI⁻ photoelectron spectrum using the BP Br + HI LEPS surface reduce some discrepancies found between experiment and the earlier collinear simulation.⁸ Finally, a three-dimensional surface has been constructed for the Br + HBr reaction by extending the earlier fitted collinear surface⁵ to three dimensions. Adiabatic calculations on this surface accurately reproduce the experimental BrHBr⁻ and BrDBr⁻ photoelectron spectra.

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