Rotational Distributions in the Photodetachment of IHI\(^-\) and in the I + HI Reaction:  
The Influence of IHI Transition State Resonances

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Abstract. Franck–Condon factors which determine IHI\(^-\) photodetachment spectra have been calculated using a three-dimensional coupled-channel reactive scattering program. These Franck–Condon factors show peaks as a function of energy that are in reasonable agreement with measured spectra due to Neumark and co-workers. Some of these peaks are due to IHI transition state resonances and others are due to direct scattering reactive threshold effects. An analysis of the rotational distributions associated with the Franck–Condon factors indicates that when direct scattering is dominant, the distributions peak at the rotational state which is nearest to its effective reaction threshold. At energies where IHI transition state resonances are important, the rotational distribution changes, thus providing a characteristic signature of resonance formation. The I + HI bimolecular rotational distributions are also considered, and they also show important differences between direct and resonant energies.

1. INTRODUCTION  
One of the most important results of early quantum scattering studies of collinear atom plus diatomic molecule reactions (i.e., \(H + H_2\)) was the observation\(^1\) of peaks and dips in reaction probabilities that are due to metastable states (resonances) localized near the transition state region of the reactive potential energy surface. This discovery stimulated intense theoretical activity, both from the point of view of characterizing the reactive resonances (as reviewed in Ref. 4) and for the purpose of identifying candidates for experimental study. Very recently there have been experimental measurements consistent with the observation of reactive resonances,\(^5\) thus providing hope that real pay-offs may finally be achieved from all of this theoretical work.

One of these recent experiments is that by Weaver et al.\(^7\) on the photodetachment of IHI\(^-\). The neutral IHI which is produced during photodetachment in these experiments corresponds to the transition state of the iodine plus hydrogen iodide (I + HI) reaction, and what Weaver et al. see are peaks in the photodetachment spectra suggestive of resonances in the transition state region of I + HI. However, these experiments need to be interpreted with care, for as we shall see below, other effects besides resonances can be responsible for the peaks. This makes further theoretical work highly desirable, and the present paper is intended with this in mind, with the specific goal of seeing what characteristic signatures of resonance formation can be found in the rotational distributions associated with photodetachment spectra and bimolecular reaction probabilities.

I + HI has actually been of interest to theoreticians for a long time.\(^8\)–\(^10\) Early interest in this reaction arose from its special mass combination, as it posed an important challenge to the development of quantum scattering methods\(^8\) and it also provided an example of exceptional vibrational adiabaticity\(^8\),\(^10\) that could be described accurately by simple analytical theories.\(^9\) Subsequently, it was suggested by Pollak\(^11\) and confirmed by Manz et al.\(^12\) that collinear IHI can have

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bound states even though the potential surface has no minima. These bound states occur as a result of vibrationally adiabatic stabilization of the transition state region, and Manz et al. found four such bound states on a LEPS (London–Eyring–Polanyi–Sato) surface that was developed by Manz and Römelt\(^{10}\) (their "surface A," which will be denoted MRA). The discovery of bound states for collinear IHI precipitated several studies of three-dimensional bound states,\(^{13,14,16}\) and one such bound state was found on the MRA surface by Pollak\(^{13}\) using semiclassical methods, and by Clary and Connor\(^{14,16}\) and Bowman and Gazdy\(^{20}\) using quantum variational methods. However, it appears from the measurements of Weaver et al.\(^{7}\) that there are no real IHI bound states and that the theoretical conclusions were based on an inaccurate potential energy surface. Interest in the I + HI reaction has shifted recently to the study of resonance states. Both Clary and Connor\(^{14,16}\) and Bowman and Gazdy\(^{20}\) have calculated energies of several of the lowest resonance states, and Bowman and Gazdy have calculated photodetachment Franck–Condon factors in one and three dimensions, using an adiabatic bend approximation to generate the three-dimensional results. In addition, there has been recent work by Pollak\(^{13}\) and by Skodje and Davis\(^{19}\) on studying the phase space structure of the collinear classical reaction dynamics, with an emphasis on understanding both resonance formation and the oscillating reaction probabilities that are observed in direct scattering. Reviews of work on IHI may be found in Refs. 17 and 18.

Recently, Schatz\(^{21}\) has calculated photodetachment Franck–Condon factors for IHI\(^{-}\), using a coupled-channel three-dimensional hyperspherical reactive scattering method to generate the final state continuum wavefunctions. This Franck–Condon factor is given by

\[
S_d = \left| \langle \chi_i | \psi_r^- \rangle \right|^2, \tag{1}
\]

where \(\chi_i\) is the initial vibration/rotation wavefunction of IHI\(^{-}\) and \(\psi_r^-\) is the IHI scattering wavefunction that satisfies outgoing wave boundary conditions in channel \(f\) as \(t \to \infty\). The measured photodetachment spectra do not resolve final HI vibration/rotation states, so comparison with experiment involves calculating the sum

\[
S(E) = \sum_f S_d, \tag{2}
\]

where we have suppressed the index \(i\) on the left hand side.

Figure 1 presents a plot of the calculated \(S(E)\) vs. total energy \(E\) based on the MRA potential surface.\(^{10}\) (Details of the calculations will be summarized below.)

This figure has a lot of structure, but only some of the peaks correspond to transition state resonances (as can be determined by examining plots of scattering wavefunctions). In particular, Schatz found that the sharp spike at 0.1495 eV and a barely discernable spike at 0.1595 eV are due to resonances, with quantum numbers (symmetric stretch, bend, antisymmetric stretch) = (100) and (200), respectively. Also, the spikes at 0.340, 0.353, 0.368, and 0.380 eV are due to resonances with quantum numbers (002), (102), (202), and (302). The other peaks correspond to direct reactive scattering rotational thresholds where the inner translational turning point during I + HI collisions occurs close to an effective adiabatic barrier for reaction. Since the scattering wavefunction is always large near turning points and since the Franck–Condon region overlaps closely with where many of these adiabatic barriers are located, the Franck–Condon factors are large near thresholds even though the scattering is direct.

The theoretical spectrum shown in Fig. 1 is in reasonable but not perfect agreement with experiment as shown in Fig. 2. Here the theoretical spectrum has been averaged with a 30 meV Gaussian to simulate experimental broadening (actually this is an overestimate that we have deliberately chosen so as to make the spectrum simple), and the experimental spectrum has been shifted down by 0.08 eV to make the energies of the lower energy experimental peak match with the calculated peak (presumably to correct for deficiencies in the potential surface and for experimental uncertainties in the energy origin). The resulting figure shows that the calculated energy of the second peak matches closely with experiment, as do the widths of both peaks. (Here it should be noted that the peak widths are much larger than the assumed 30 meV Gaussian.)

An important conclusion from this theoretical analysis of the IHI\(^{-}\) photodetachment spectrum is that not all peaks in the experimental spectrum are due to resonances. The second peak in Fig. 2 arises mostly from resonances, but the first peak is due mostly to direct scattering. Thus it appears that a careful theoretical analysis of photodetachment spectra will be needed to decide whether or not resonances are being observed.

In this paper, we would like to analyze the rotational distributions associated with photodetachment spectra to see what further information they provide, and especially if they are noticeably different on and off resonance. We will also consider how the Franck–Condon photodetachment rotational distributions compare with bimolecular rotational distributions, and we will study the energy dependence of both kinds of
rotational distribution. Although there are no experiments yet on either distribution, we hope that the present paper will stimulate interest in this topic, as it does appear that valuable information can be obtained.

2. CALCULATIONS

Most of the details of the calculations were described in Ref. 21 or in an earlier paper on CIHCl photodetachment, so only a summary is given here. The quantity of interest in this paper is the Franck-Condon factor $S_q$ defined by Eq. (1). In the present calculation, $\chi_i$ is always taken to be the ground vibration/rotation state of the negative ion, so we drop the index $i$ in what follows. $\psi_{\text{f}}$ is the reactive scattering wavefunction of the neutral, and is labelled by the energy $E$, the total angular momentum $J$, and the final vibration/rotation quantum numbers $v$, $j$, so we use the notation $\psi_{vj}^f(E)$ instead of $\psi_{\text{f}}$. In this case Eq. (1) becomes:

$$ S_{vj}^f(E) = |\langle \chi | \psi_{vj}^f(E) \rangle|^2. \tag{3} $$

For the present calculations, $J$ has always been chosen to be zero (corresponding to the Q branch of the rotational spectrum starting from the ground state). We will see in the next section that the HI rotational distributions are generally dominated by high rotational states ($j > 10$) produced as a result of repulsion between I and HI while the fragments separate, so it is unlikely that other rotational branches (which would involve addition or subtraction of one or two units of angular momentum to the IHI intermediate) will produce rotational distributions that differ much from what we have calculated.

To describe the wavefunction $\chi$, we use a rigid rotor/harmonic oscillator approximation, with parameters given in Ref. 21. The final state wavefunction $\psi_{vj}^f(E)$ is obtained from a coupled-channel reactive scattering calculation based on the hyperspherical coordinate method described in Ref. 23. The MRA potential surface is used for all calculations. Numerical details of these calculations are given in Ref. 21.

A number of sophisticated methods now exist for evaluating Franck-Condon factors for bound to continuum transitions indirectly without having to construct the scattering wavefunction, but in the present calculation we have evaluated the Franck-Condon factors directly by numerical quadrature. This is not too inefficient in this application, since the integrand in Eq. (3) is both smooth and simple. Note that the two $P$'s are assumed distinguishable in this calculation, thereby ignoring possible interference oscillations that might occur if the wavefunction were properly antisymmetrized. Any reasonable amount of energy averaging is expected to wash out such oscillations.

The reactive scattering calculations have used a basis of 22 states per arrangement channel at low energy (\( \leq 0.17 \, \text{eV} \)), and 32 at higher energy, with the latter basis consisting of 16, 10, and 6 rotations for $v = 0$, 1, and 2, respectively. Convergence of the calculation based on the usual criteria of invariance with respect to basis set and converged symmetry and unitarity, is excellent below 0.30 eV, but above that energy the results are not fully converged, with unitarity good to

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only 5%. In spite of this, the results are expected to be qualitatively accurate at high energy, and this is adequate for this study since the potential surface has important deficiencies that make it impossible to obtain quantitative results.

3. RESULTS

3.1. Choice of Energies

Eleven values of the total energy $E$ (relative to $^{1}+\text{HI}$ with $I$ at equilibrium) have been selected at which to calculate rotational distributions. Referring to Fig. 1, these energies are: 0.14945, 0.155, 0.165, 0.200, 0.230, 0.300, 0.330, 0.340, 0.345, 0.353, and 0.362 eV. The lowest of these energies coincides with the (100) resonance, while the next five are energies where it is felt that direct scattering is dominant. The 0.340 and 0.353 eV energies correspond to resonances which are important in the photodetachment spectrum, while 0.330, 0.345, and 0.362 eV correspond to energies close to these resonances but still far enough away that direct scattering is dominant. For each energy we have calculated $J = 0$ Franck-Condon factors and bimolecular reaction probabilities. Since the only open vibrational state at these energies is $v = 0$, the Franck-Condon factors only depend on the final HI rotational quantum number $j$ and on $E$, so we use the symbol $S_{j}(E)$ instead of $S_{0j}(E)$. Likewise, the $^{1}+\text{HI}$ reaction probability will be denoted by $P_{j}(E)$, where $j'$ is the initial and $j$ the final rotational quantum number.

3.2. Franck-Condon Rotational Distributions

Figure 3 presents the Franck-Condon factor $S_{j}(E)$ vs. $j$ for the 11 energies chosen. Each plot has been separately normalized to a maximum value of unity, with successive curves shifted up by one unit for visual clarity.

Figure 3 shows that the rotational distributions are for the most part remarkably simple, with usually a single state responsible for nearly all of the intensity. The $j$ value associated with this state equals 0, 1, 2, 7, 9, 12, 14, 14, 14, 13, and 15 for the 11 energies plotted (using the order given in the figure caption). For most energies, this $j$ value is close to the highest allowed by energy conservation. This can be inferred by noting where each curve stops since this $j$ value is the highest allowed at each energy.

Notice that as we scan through the resonances at 0.340 and 0.353 eV, there are sudden changes in the rotational distributions. At $E = 0.330$ eV, the distribution is typical of direct scattering, with a single rotor state ($j = 14$) being dominant, but at 0.340 eV, a second peak at $j = 12$ has grown in. This $j = 12$ peak is smaller than that at $j = 14$ at $E = 0.340$ eV, but it is larger at $E = 0.341$ eV (not shown) which is also within the resonance width. However, the $j = 12$ peak disappears at 0.345 eV, and the distribution looks direct again. Then, at 0.353 eV, the distribution shifts down suddenly to peak at $j = 13$, while at 0.362 eV, the distribution looks like direct scattering again, with a peak at $j = 15$. The shift from a direct peak at $j = 14$ to one at $j = 15$ as one goes from 0.330 eV to 0.362 eV is the expected change based on direct scattering threshold effects. Thus, the effect of the resonances is either to cause additional lower $j$ peaks to appear, or to shift the peak of the distribution to lower $j$.

3.3. Bimolecular Rotational Distributions

Figure 4 presents the bimolecular reaction probability $P_{j'}$ vs. $j$ at the 11 energies, with $j'$ chosen as the rotational state where $\Sigma_{j} P_{j}$ exhibits a peak as a function of $j'$. At all energies other than 0.340 and 0.353 eV, this sum has just one peak as a function of $j'$, but at these two resonance energies there are multiple peaks, and we have selected the highest $j'$ peak to make the plot. This highest $j'$ peak occurs at $j' = 1, 2, 3, 6, 8, 9, 12, 12, 13, 13, and 12$ for the 11 energies plotted. Note that for each energy we have separately normalized the probabilities to a maximum value of unity, and we have shifted the curves as in Fig. 3, so that Figs. 3 and 4 can be directly compared.

Figure 4 shows that the reaction probabilities for $E \leq 0.3$ eV (i.e., the lowest six curves) all have a single dominant peak, much like the Franck-Condon peak in Fig. 3, although the Franck-Condon peak usually occurs one or two units of angular momentum higher than the reaction probability peak, and usually the Franck-Condon peak is narrower. The peaks in the rotational distribution occur at $j = 1, 2, 3, 6, 8$, and 10 for $E = 0.14945, 0.155, 0.165, 0.200, 0.230$, and 0.300 eV, respectively. These $j$ values are identical to (or differ by at most one unit of angular momentum from) the peak $j'$ values given above, indicating a strong $j = j'$ propensity. However, it should be noted that the rotational distributions for $j'$ values other than the peak do not show the same propensity. In fact, the $^{1}+\text{HI}$ rotational distributions are (at energies above 0.200 eV) like
Fig. 3. Franck–Condon factor $S_j(E)$ vs. $j$ for $E = 0.14945$ (solid curve at bottom), 0.155 (dash–dot), 0.165 (long dash–short dash), 0.200 (short dash), 0.230 (dots), 0.300 (solid), 0.330 (dash–dot), 0.340 (long dash–short dash), 0.345 (short dash), 0.353 (dots), and 0.362 eV (solid curve at top). Note that each curve has been normalized to a maximum value of unity, and successive curves have been shifted up by one unit for visual clarity.

Fig. 4. I + HI reaction probability $P_{j'j}(E)$ vs. $j$ for the same 11 energies that were considered in Fig. 3, and using the same normalization and shifting of successive curves. $j'$ is the rotational state for which the sum over $j$ of $P_{j'j}$ shows its highest $j'$ maximum for each energy considered.

what Schatz et al. found in studying CI + HCl with very high product rotational excitation that is not strongly correlated with the initial rotational state.

Now consider the top five energies in Fig. 4. At 0.330 eV, the distribution peaks at $j = 10$, but a second peak at $j = 12$ has started to grow in. At the resonance energy of 0.340 eV, the distribution suddenly shifts to a single peak at $j = 11$. Then, at 0.345 eV, the distribution has reverted to what it looked like at 0.330 eV, with peaks at $j = 10$ and 12. Going up to the resonance at 0.353 eV, we see a single peak at $j = 11$ much as occurs at 0.340 eV, but then at 0.362 eV we see a bimodal distribution that is closely related to what is seen at 0.345 eV.

Overall we see substantial changes in the rotational distributions in Fig. 4 as we tune through the resonances at 0.340 and 0.353 eV, with the distributions being oscillatory away from resonance, then sharpening up on resonance. These changes are quite different from what happens to the Franck–Condon factors, although the strong energy dependence of the distributions is common to both.

4. DISCUSSION

The important result of our analysis of photodetachment and bimolecular rotational distributions is that these distributions undergo important changes at certain energies that provide a signature for formation of resonances. At energies where direct scattering is dominant, the rotational distributions in either Fig. 3 or Fig. 4 are often very simple, with a single rotational state being dominant. For the bimolecular reaction probabilities, the dominant final state is always the same as or close to the dominant initial state (i.e., $j' = j$). The $j' = j$ propensity does not, however, hold for $j'$ values other than the dominant state.

These conclusions concerning the direct scattering results are consistent with the analysis of Ref. 21, which found that both Franck–Condon factors and reaction probabilities are dominated by rotational threshold effects. Except at low energies ($\lesssim 0.2$ eV), the rotor states involved are high enough that rotation tends to be adiabatic for the state that is close to threshold (hence the $j' = j$ propensity). In Ref. 21 it was also found by examining plots of wavefunctions that the Franck–Condon factor peaks at a lower energy than does the reaction probability for the rotational state that is near threshold. This is due to the fact that the Franck–Condon region is located at larger H–I distances than the saddle point, so as the energy is increased, the wavefunction of the state near threshold penetrates first to the Franck–Condon region (producing a big Franck–Condon factor) and then to the saddle point (producing a big reaction probability). In the present analysis, this shows up as a peak in the Franck–Condon rotational distribution that occurs at higher $j$ for each $E$ than that in the reactive rotational distribution.

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At the higher energies where direct scattering is still dominant (0.330, 0.345, and 362 eV), Fig. 4 shows that the reaction probabilities have multiple peaks. This sort of behavior has been seen in other contexts in the past, such as in H + CO rotationally inelastic scattering calculations by Lee and Bowman, and in similar model calculations by McCurdy and Miller. In both of these calculations, oscillations in the \( J = 0 \) rotational distributions were attributed to interference between scattering off the two nearly identical ends of the CO molecule. Although \( I + HI \) is clearly very different from \( H + CO \), the concept of interference between different paths may still be the origin of the oscillatory rotational distributions. In particular, it is known from studies of \( CI + HCl \) that heavy + light–heavy reactions can occur by distinctly different types of trajectories that produce products with different rotational distributions. One type of trajectory involves a nearly collinear encounter that leads to rotationally cold products, while the other involves a “figure eight” trajectory that produces rotationally hot products. At low energies, only the nearly collinear trajectories are encountered, but at high energies both can occur, and interference between them may be responsible for the oscillatory rotational distributions. Presumably these oscillations are not seen in the Franck–Condon factors because only the high rotational excitation pathway is close enough to threshold to make the wavefunction big in the Franck–Condon region.

The mechanism underlying the change in rotational distribution that occurs close to the resonance is more subtle, and only a rough picture can be given. Figure 3 shows that close to resonance the rotational distribution either shifts in \( j \) or grows new peaks. Since the Franck–Condon factor is very sensitive to how the resonance wavefunction in the interaction region relates to the asymptotic internal states (i.e., how the resonance decays), the distributions seen in Fig. 3 imply that the resonance can decay into one or more states which are different from those which control the direct scattering Franck–Condon factors.

Given that the resonant Franck–Condon factors in Fig. 3 can have multiple peaks, it might seem surprising that the resonant reaction probabilities in Fig. 4 have just one peak, but it should be remembered that in contrast to Fig. 3, Fig. 4 refers to a single initial rotational state for each energy. This rotational state is that for which the reaction probability peaks, and it should be noted that for lower rotational states much removed from this state, the rotational distributions show multiple peaks that are similar to what we see at energies where only direct scattering occurs. This indicates that it is only rotational states close to where the probability peaks that are strongly perturbed by the resonance.

Some guidance as to what is happening can be extracted from the work of Lee and Bowman on \( H + CO \). They found that close to resonance, the oscillatory rotational distributions that they observed away from resonance sharpened into a single-peaked distribution. They attributed this behavior to the fact that the resonance is populated by only one of the two possible collision paths mentioned above, namely collisions of \( H \) with the C end of the CO molecule. If only one path is important, interference between the paths doesn’t occur and the rotational distributions that result are smooth. This argument would apply to our case if only one of the two possible trajectories that we discussed above (collinear and “figure eight”) were strongly coupled to the resonance. Given the dominance of high rotor excitation in the results, it seems likely that it is the “figure eight” trajectory that is coupled to the resonance. Then, for the lower initial rotational states to which the resonance is not coupled, we recover the multiple-peaked distributions characteristic of direct scattering involving multiple reaction paths.

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REFERENCES


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