Probing Excited Electronic States Using Vibrationally Mediated Photolysis: Application to Hydrogen Iodide†

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We measure branching ratios and anisotropy parameters for the photolysis of HI(ν=2,J=0) → H + I(2P°,v2)/I(2P°,v2) over the wavelength range 297–350 nm. HI is prepared in the ν = 2, J = 0 rovibrational level using direct IR absorption, and the H-atom photofragments are probed with resonance enhanced multiphoton ionization coupled with core-extraction time-of-flight mass spectrometry. The new branching ratio measurements disagree with predictions obtained from ab initio calculations and from the results of an empirical analysis based on experimental values of the HI/DI(ν=0) absorption cross sections and branching ratios. Thus, we combine our new data with all existing absorption coefficient and branching fraction data for HI/DI in a global analysis that provides a new empirical determination of the final-state potential curves and transition moment functions for the four excited electronic states contributing to the A-band UV absorption continuum of HI. This analysis yields two models for the radial dependence of the excited state potential energy curves and transition dipole moment functions. The existing data cannot differentiate these models, but this work identifies a range of experiments that would do so. More generally, we demonstrate that photodissociation of vibrationally excited molecules is a sensitive probe of the repulsive excited electronic states encountered in bound-free transitions.

I. Introduction

Consider the unimolecular dissociation of a molecule when it absorbs a photon with sufficient energy to cleave a bond: the mechanism of this process and the resulting products are subtle probes of the forces at work in the excited electronic state or states prepared by the radiation field. Determining the mechanism and the photodissociation products, however, is not a trivial task, because several dissociation channels are often available. Questions that often arise include: what photofragments are formed? In what quantum states are they formed? What are the product vector correlations of these states; e.g., how does the velocity of the recoiling fragment point with respect to the direction of linear polarization of the light beam? In 1971 Jonah, Chandra, and Bersohn1 used a method of “photolysis mapping” to begin addressing these very questions in the photolysis of Cd(CH3)2. The anisotropy of the Cd atoms with respect to the electric vector of the photolysis light was measured by allowing Cd to deposit on a glass hemispherical cell. From these measurements Bersohn and co-workers succeeded in making the first determination of the photoproduction angular distribution. They were able to conclude that the transition moment must be perpendicular to the C−Cd−C molecular axis of Cd(CH3)2.

This experiment and others confirmed that the photofragment angular distribution from a one-photon photodissociation event using linearly polarized light is given by2,3

\[ I(\theta) = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta)] \]  

where \( \theta \) is the angle between the electric vector of the light and the velocity vector of the product, \( \sigma \) is the partial cross section for the dissociation product, \( P_2(s) \) is the second-order Legendre polynomial, and \( \beta \) is the anisotropy parameter. Within the axial recoil approximation, \( \beta = -1 \) corresponds to a perpendicular transition whereas \( \beta = +2 \) corresponds to a parallel transition. Since these early investigations, the union of detailed, high-quality experimental data with the most recent theoretical calculations has deepened our understanding of the immense complexities associated with the seemingly simple processes involved in molecular photodissociation.

In recent reviews, Crim4,5 describes the power of vibrationally mediated photodissociation6 to influence the outcome of a photodissociation event and unravel the complex interactions in the excited electronic states. Furthermore, as Figure 1 illustrates for the specific case of HI, vibrational excitation of molecules in the ground electronic state is a simple way to explore regions of the potential energy surface that are normally inaccessible. Although the information provided by such experiments should be a stringent test of available theories and enhance our understanding of excited electronic states, only a few studies7–9 have considered the effect of vibrational excitation on the photodissociation dynamics of HX molecules. Such investigations are important to provide a testing ground for concepts that

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might be applied to larger molecules. For example, what similarities can be drawn between photodissociation spectra of the HX series and the analogous CH$_2$X series? They also continue a long tradition of spectroscopic studies of the ground and excited electronic states of the hydrogen halides.

The hydrogen halides, HX (X = F, Cl, Br, I), are prototypical systems for investigating photodissociation dynamics because they provide an opportunity to explore nonadiabatic effects as well as the increasing spin–orbit coupling and decreasing bond strength from HF to HI. Excitation of HX molecules in the A-band continuum yields two different dissociation channels:

$$\text{HX} \rightarrow \text{H} (^2S) + \text{X} (^2P_{3/2})$$  \hspace{1cm} (2)

$$\text{HX} \rightarrow \text{H} (^2S) + \text{X}^* (^2P_{1/2})$$  \hspace{1cm} (3)

Here, we follow the standard convention of labeling the ground state ($^2P_{3/2}$) halogen atoms by X, and the spin–orbit-excited atoms ($^2P_{1/2}$) by X$^*$. The branching ratio between these channels has been the subject of numerous experimental and theoretical investigations for HF, HCl, HBr, and HI. This ratio is often expressed in terms of $\Gamma$, which is defined as

$$\Gamma = \frac{\Phi_{X^*}}{\Phi_X + \Phi_{X^*}}$$  \hspace{1cm} (4)

where $\Phi_X$ and $\Phi_{X^*}$ are the quantum yields of X$^*$ and X, respectively. Experimentally, the photolysis of HI has received the most attention of the halogen halides, in part because the A-band absorption spectrum is red-shifted to more accessible wavelengths.

A. HI($\nu=0$) Photodissociation. The UV absorption spectrum of HI is broad and featureless, with the A-band beginning around 300 nm, peaking at $\sim$220 nm, and decreasing before the beginning of the B-band around 200 nm. In 1937 Mulliken predicted that the observed A-band absorption was the result of Q $\rightarrow$ N transitions, where N represents the $^3\Sigma^+$($0^+$) ground state and Q represents the group of states: $^3\Pi(1)$, $^1\Pi(1)$, and $^3\Pi(0^+)$. Although he also considered transitions to the T $^3\Sigma^-$ ($1$ and V $^1\Sigma^+$($0^+$) states, he predicted that the V state would show discrete band structure and that both the T and V states would be important only at higher energies. The empirically derived potential energy surfaces of the N, Q, and T levels are shown in Figure 1. Here, we retain the historical Hund’s case (a) notation but give $\Omega$ in parentheses because the presence of the heavy I atom results in a large spin–orbit splitting, which suggests that a Hund’s case (c) description is likely better. In addition, we follow the convention of labeling triplet states with lower case letters, which was not used by Mulliken. The $^3\Pi$($0^+$) $\rightarrow$ X $^1\Sigma^+$($0^+$) transition is a parallel transition ($\Delta\Omega = 0$) and correlates to the H + I$^*$ channel, whereas the other two Q $\rightarrow$ N transitions, a $^3\Pi(1) \rightarrow$ X $^1\Sigma^+$($0^+$) and A $^1\Pi(1) \rightarrow$ X $^1\Sigma^+$($0^+$), are both perpendicular transitions ($\Delta\Omega = \pm 1$) and correlate to the H + I channel. Finally, the T $^3\Sigma^+$(1) $\rightarrow$ X $^1\Sigma^+$($0^+$) continuum at the blue end of the A-band is a perpendicular transition and correlates to the H + I$^*$ channel.

Although early attempts to measure the branching ratio $\Gamma$ were made using photochemical methods, the uncertainties in such indirect techniques were rather large. After these initial measurements, numerous other groups made measurements of $\Gamma$ and the spatial anisotropy parameter for the I and I$^*$ channels, i.e., $\beta$ and $\beta^*$, at a variety of wavelengths in the A-band. These measurements were generally consistent with Mulliken’s prediction that I atoms arise from a perpendicular transition whereas I$^*$ atoms are formed only via a parallel transition, except at the blue end of the A-band where a perpendicular transition into the T $^3\Sigma^+$(1) state grows in. Figure 2 summarizes the extensive experimental measurements and displays the most recent ab initio calculations along with the results of a comprehensive empirical analysis by Le Roy et al. The ab initio calculations of the branching ratios agree qualitatively with the experimental values, whereas the empirical analysis agrees quantitatively. We note that unlike the previous theoretical work of Levy and Shapiro, the studies mentioned here did not include nonadiabatic couplings, a point that will be addressed in more detail later.

Figures 1 and 2. Experimental measurements and theoretical calculations of the branching ratio $\Gamma$ for HI($\nu=0$) photolysis. For clarity, no attempt is made to differentiate the experimental measurements (●) from refs 27–29, 31–33, 36–40, and 42. The dashed line represents ab initio calculations from ref 41, and the solid line is from the empirical analysis of ref 43.
excited-state potentials and transition dipole moment functions that are probed in this work.

Experimentally, the photodissociation dynamics of vibrationally excited HX molecules have been mostly neglected with a few exceptions: Zhang et al. determined $\Gamma$ for the 193.3 nm photolysis of HF ($\nu=3$); Regan et al. measured $\Gamma$ for the photodissociation of HCl ($\nu=1, J=0.5$), HCl ($\nu=2, J=0.11$), and HCl ($\nu=3, J=0.7$) at $\sim 235$ nm; and Zittel and Little compared the relative absorption cross-sections of HBr ($\nu=1$) and HBr ($\nu=0$) at 258.9 nm. These measurements indeed show that vibrational excitation can be a significant factor in the photodissociation process.

In this article, we report values of $\Gamma$, $\beta$, and $\beta^*$ for vibrationally excited HI molecules, despite the extensive effort that has been made to obtain accurate values for the excitation energy dependence $\epsilon$ (molar absorption coefficients), $\Gamma$, $\beta$, and $\beta^*$ for HI/DI ($\nu=0$).

II. Methods and Procedures

A. Experimental Details. Figure 3 shows a schematic of the experimental apparatus, which has been described in detail elsewhere. Here we present only a brief summary of the instrument and details important to the current experiments. A 1:20 mixture of hydrogen iodide, obtained by standard synthetic procedures, and helium (Liquid Carbonic, 99.995%) is expanded from a pulsed nozzle (General Valve, Series-9) into the extraction region of a linear Wiley–McLaren time-of-flight (TOF) spectrometer. The state preparation, photolysis, and product detection are accomplished using three different laser beams that intersect the expansion approximately 1 cm below the nozzle orifice. HI is first prepared in the $\nu=2$, $J=0$ level by direct IR absorption near 2.3 $\mu$m. The IR light, focused by a $f = 65$ cm CaF$_2$ lens into the extraction region, is generated by difference frequency mixing, DFM, and optical parametric amplification, OPA. The photolysis and probe light is generated by frequency doubling in BBO the output of a dye laser. The IR is generated by frequency doubling in BBO the output of a dye laser. The photolysis beam dissociates the faster moving products flying out of the detection region.

The branching ratio and anisotropy parameters are obtained using the well-established core-extraction technique coupled with space-focused TOF mass spectrometry. In this technique the ions are allowed to spread in time according to their initial velocities. Ions with velocity components perpendicular to the flight axis are rejected by the core extractor to simplify the data analysis. The mass spectrometer extraction voltages are set at 20 V/cm to give a resolution of $\sim 1300$ m/s for the H atom, which is sufficient to resolve the different dissociation channels. The direction of the linearly polarized photolysis beam is rotated between parallel and perpendicular to the TOF axis on an every-other-shot basis using a photoelastic modulator (PEM-80, Hinds International Inc). The resultant signals are combined to give the isotropic, $I_{iso} = 2I_{\parallel} + I_{\perp}$, and anisotropic, $I_{aniso} = 2(I_{\parallel} - I_{\perp})$, TOF profiles, which are related to the speed-dependent population and speed-dependent lab-frame spatial anisotropy, $\beta(v)$, of the ions, respectively. The purity of the photolysis polarization is confirmed by placing a polarizer after the PEM.
because under perfect core-extraction conditions, relative peak areas of the isotropic and anisotropic profiles studied. Similar data are obtained for the other wavelengths (d), moving initially toward and away from the detector, displays the isotropic and anisotropic core-extracted TOF profiles.

As a check on our fitting program, we also calculate the overlap region, blue region of the A-band absorption. Thus, we choose to retain the new basis functions generated by a Monte Carlo simulation 50 to obtain the lab-frame speed distribution and \( \alpha \) or four basis functions for the A 1\( \Pi \) state, which is only significant in the extreme overlap region, middle of the Franck-Condon overlap region, \( r_x = 1.609 \, \text{Å} \), and the exponent coefficient \( \beta(r_x) = \beta_0 + \beta_y r_x + \beta_2 r_x^2 + \ldots \) is defined as an expansion in the dimensionless radial variable \( r_p = [r^p - r_c^p]/[r^p + r_c^p] \). In the EMO function, eq 7, \( \partial_s \) is the well depth and \( r_c \) is the radial position of the shallow minimum. Because this predicted shallow potential minimum is outside the region probed by HI(\( v=0 \)) photodissociation studies, \( \partial_s \) is fixed at the ab initio value \( \partial_s = 600 \, \text{cm}^{-1} \). Similarly, without further experimentation we fix the power defining the radial distance variable as \( y_p(r) \) with \( p = 8 \).

In earlier work 43 the photodissociation spectra originating in a \( v = 0 \) vibrational level was found to be quite insensitive to the radial shape of a transition dipole moment function because of intimate correlation with the position and shape of the final-state potential curve. This restriction is lifted, however, if the data depend significantly on absorption from vibrationally excited levels. As a result, we consider two types of models: (1) the transition moment functions are linearly scaled versions of the ab initio functions,43 and (2) the transition moment functions are represented by empirical expansions in powers of the radial variable \( y_p \).

We cannot expect that the current data, lying at the red end of the photolysis region, will give new insight regarding transitions to the \( 2\Sigma^+ \) state, which is only significant in the extreme blue region of the A-band absorption. Thus, we choose to retain.

Table 1: Experimental Values for the Branching Ratio \( \Gamma \) and Anisotropy Parameters \( \beta \) and \( \beta^* \) for HI(\( v=2,J=0 \)) Photolysis

<table>
<thead>
<tr>
<th>wavelength (nm)</th>
<th>( \Gamma ) (( \pm 0.05 ))</th>
<th>( \beta ) (( \pm 0.05 ))</th>
<th>( \beta^* ) (( \pm 0.05 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>297</td>
<td>0.64 ± 0.05</td>
<td>-0.93 ± 0.12</td>
<td>2.08 ± 0.12</td>
</tr>
<tr>
<td>306</td>
<td>0.76 ± 0.04</td>
<td>-0.99 ± 0.12</td>
<td>1.96 ± 0.22</td>
</tr>
<tr>
<td>313.88</td>
<td>0.80 ± 0.04</td>
<td>-0.96 ± 0.12</td>
<td>2.03 ± 0.26</td>
</tr>
<tr>
<td>320</td>
<td>0.79 ± 0.06</td>
<td>-0.93 ± 0.15</td>
<td>1.97 ± 0.12</td>
</tr>
<tr>
<td>330</td>
<td>0.81 ± 0.05</td>
<td>-1.09 ± 0.26</td>
<td>1.80 ± 0.23</td>
</tr>
<tr>
<td>340</td>
<td>0.61 ± 0.05</td>
<td>-1.10 ± 0.17</td>
<td>1.84 ± 0.20</td>
</tr>
<tr>
<td>350</td>
<td>0.26 ± 0.04</td>
<td>-1.05 ± 0.11</td>
<td>1.95 ± 0.12</td>
</tr>
</tbody>
</table>

* The stated uncertainty is the statistical 95% confidence interval calculated from replicate measurements.

1. Thus, only a brief description of the theoretical methods is provided. The analysis is based on a quantum mechanical simulation of the total absorption coefficient and branching ratio data. A least-squares fitting procedure optimizes the parameters characterizing the analytic models for the various final-state potential energy functions.

Following the approach of ref 43, the potential energy functions for the \( A \, ^1\Pi(1) \), \( a \, ^1\Pi(1) \), and \( t \, ^2\Sigma^- (1) \) states are represented by the simple exponential function

\[
V_{\text{exp}}(r) = \beta_s + A_s e^{-\beta_s (r-r_c)}
\]

and the \( a \, ^3\Pi(0^+) \) state is represented by the "extended Morse oscillator" (EMO) function

\[
V_{\text{EMO}} = [ \beta_s - \beta_c ] + A_s e^{-\beta_s (r-r_s)} - 1^2
\]

Here, \( \beta_s \) is the energy at the asymptote of electronic state \( s \), \( r_s \) is a reference distance chosen to lie near the ground-state equilibrium distance in the middle of the Franck-Condon overlap region, \( r_s = 1.609 \, \text{Å} \), and the exponent coefficient

\[
\beta(y_p) = \beta_0 + \beta_y y_p + \beta_2 y_p^2 + \ldots
\]

is defined as an expansion in the dimensionless radial variable \( y_p = [r^p - r_c^p]/[r^p + r_c^p] \). In the EMO function, eq 7, \( \beta_c \) is the well depth and \( r_c \) is the radial position of the shallow minimum. Because this predicted shallow potential minimum is outside the region probed by HI(\( v=0 \)) photodissociation studies, \( \beta_c \) is fixed at the ab initio value \( \beta_c = 600 \, \text{cm}^{-1} \). Similarly, without further experimentation we fix the power defining the radial distance variable as \( y_p(r) \) with \( p = 8 \, 43 \).

In earlier work 43 the photodissociation spectra originating in a \( v = 0 \) vibrational level was found to be quite insensitive to the radial shape of a transition dipole moment function because of intimate correlation with the position and shape of the final-state potential curve. This restriction is lifted, however, if the data depend significantly on absorption from vibrationally excited levels. As a result, we consider two types of models: (1) the transition moment functions are linearly scaled versions of the ab initio functions,43 and (2) the transition moment functions are represented by empirical expansions in powers of the radial variable \( y_p \).

\[
M(r) = \sum_{i=0}^{\infty} c_i y_p^i
\]

We cannot expect that the current data, lying at the red end of the photolysis region, will give new insight regarding transitions to the \( 2\Sigma^- \) state, which is only significant in the extreme blue region of the A-band absorption. Thus, we choose to retain.
the scaled ab initio TMF for the t $3\Sigma^+$ state with the scaling factor fixed at $c_0(t \ 3\Sigma^+(1)) = 1$ as in ref 43.

**III. Results and Discussion**

**A. Spatial Anisotropy.** Figure 5 displays the measured channel-specific anisotropy parameters, and Table 1 tabulates these values. Several features are immediately obvious. First, the $\beta$ values obtained for the HI$(v=2, J=0) \rightarrow H + I$ channel indicate a pure perpendicular transition within experimental uncertainty over the entire excitation energy range studied here. This result is consistent with previous studies and theoretical predictions concerning the value of $\beta^*$ for the HI$(v=0) \rightarrow H + I^*$ channel. These results have raised questions about the extent of nonadiabatic coupling present between the excited states. The recent studies of Gendron et al. and Langford et al. however, show that I* production in the A-band results from a pure parallel transition to the $a^2\Pi$ state with the scaling factor fixed at $c_0(t \ 3\Sigma^+(1)) = 1$ as in ref 43.

Figure 5. $\beta^*$ parameter for the HI$(v=2, J=0) \rightarrow H + I^*$ channel (□) and $\beta$ parameter for the HI$(v=2, J=0) \rightarrow H + I$ channel (△). Solid lines represent limiting values (−1, +2) for the anisotropy parameter $\beta$.

in the A-band results from a pure parallel transition to the $a^2\Pi(0^+)$ state. Therefore, in our opinion the available theoretical and experimental data support the current view concerning the value of $\beta^*$ for the HI$(v=0) \rightarrow H + I^*$ channel. These results have raised questions about the extent of nonadiabatic coupling present between the excited states. The recent studies of Gendron et al. and Langford et al. however, show that I* production in the A-band results from a pure parallel transition to the $a^2\Pi$ state with the scaling factor fixed at $c_0(t \ 3\Sigma^+(1)) = 1$ as in ref 43.

Several speculations consistent with the experimental data had been previously proposed. Langford et al. hypothesized that the t $3\Sigma^+$ state, predicted by Mulliken to be of higher energy than the Q group, might in fact be low enough in energy to contribute to the A-band absorption. The t $3\Sigma^+$ $(\rightarrow X^1\Sigma^+ - (0^+))$ transition is perpendicular and correlates to $I^*$ products that would lead to a nonlimiting $\beta$ parameter. In 2000 Alekseyev et al. performed an ab initio study of the excited-state potentials of HI and concluded that (1) the t $3\Sigma^+$ state would be accessible only at excitation energies greater than 50 000 cm$^{-1}$, confirming Mulliken’s initial predictions, and (2) nonadiabatic couplings are unimportant. A later study by Balakrishnan et al. explored the spin-rotational coupling of the A $^2\Pi$ and $^3\Pi$ $(0^+)$ states and found it to be negligible. Our data are consistent with this picture and further support the notion that $I^*$ production

**B. Branching Ratios.** The experimentally determined value of $\Gamma$ for HI$(v=2, J=0)$ photolysis over the range of 28000 to 34 000 cm$^{-1}$, shown in Figure 6, is very different than that observed for the HI$(v=0)$ photolysis, shown in Figure 2. Indeed, the prediction first made by Kalyanaraman and Sathyamurti, and later by other groups, that $I^*$ could be controlled by vibrational excitation is confirmed. Over the wavelength range considered here, $\Gamma$ can range from ~0.3 to 0.8, indicating that mainly $I$ or mainly $I^*$ can be produced from photolysis of HI$(v=2)$, in contrast to the photolysis of HI$(v=0)$ where the maximum value of $\Gamma$ is ~0.5 (Figure 2). To gain a deeper understanding of these differences, we now examine the relation of previous models to our HI$(v=2, J=0)$ data and as a result propose several refinements.

Figure 6 shows the predicted $\Gamma$ values derived (1) from the most recent ab initio calculations and (2) from the empirical analysis of Le Roy et al. based only on HI$(v=0)$/DI$(v=0)$ data. Although both calculations agree qualitatively with the experimental measurements of HI$(v=2)$, neither agree quantitatively. Clearly, the current potential energy curves and transition moment functions are not accurate enough to describe completely the photodissociation dynamics of HI. Consequently, we attempt to develop improved potential energy curves and transition moment functions using a comprehensive empirical analysis of all the available experimental data for HI and DI.

The resulting weighted least-squares fits (see section II.B) of the fit is represented by the dimensionless root-mean-square residual

$$\text{RMSR} = \sqrt{\frac{1}{N_d} \sum_{i=1}^{N_d} \left( \frac{Y_{\text{calc}}(i) - Y_{\text{obs}}(i)}{u(i)} \right)^2} \quad (10)$$

where $N_d$ is the number of experimental data and $u(i)$ is the estimated uncertainty in datum i. Note that one can use this quantity to indicate the quality of fit to a subset of data (such as the $v = 2, J = 0$ branching ratios) as well as for the overall

**Figure 5.** $\beta^*$ parameter for the HI$(v=2, J=0) \rightarrow H + I^*$ channel (□) and $\beta$ parameter for the HI$(v=2, J=0) \rightarrow H + I$ channel (△). Solid lines represent limiting values (−1, +2) for the anisotropy parameter $\beta$.

**Figure 6.** Branching ratio $\Gamma = \Phi_0/(\Phi_1 + \Phi_0)$ for HI$(v=2, J=0)$ photolysis plotted as a function of excitation frequency ($\omega$). Error bars represent 95% confidence limits obtained from replicate measurements. The curves are the prediction of ref 43 (dotted line), ab initio calculations from ref 41 (dashed line), and the two new models presented in this work: model 1 (dash-dot-dot line) and model 2 (solid line).
The first column of Table 2 gives the RMSR values for the entire data set, including 164 previous data points as well as the current HI\((v=2, J=0)\) measurements, obtained with the potential energy and transition moment functions determined previously.\(^{33}\) A refit of the full 14-free-parameter model used in ref 43 was performed by including the new data presented here; however, it suffered the same types of systematic discrepancies seen for the ref 43 curve in Figure 6. Thus, it is clear that obtaining good agreement with our new \(v=2, J=0\) branching ratios requires significant extensions of the best existing empirical model\(^{33}\) for this system. Therefore, fits to the full data set using a wide range of models for the final-state potentials were performed. In this phase all four transition moment functions were represented by spline functions through the ab initio points,\(^{31}\) and each was multiplied by an empirical scaling factor. However, none of these models yielded a satisfactory representation of the new \(v=2\) branching ratios. This suggested that a more sophisticated treatment of the transition moment functions, rather than of the final state potentials, was needed to match the HI\((v=2, J=0)\) measurements.

After considerable experimentation, we converged on two models defined by the parameter sets listed in Table 3, which we will refer to as models 1 and 2. The most important difference between them is that model 1 uses an empirical linear function for the transition moment function into the \(\Pi\) state and scaled ab initio functions for the others, whereas model 2 uses empirical functions linear in the variable \(y_s(r)\) for the transition moments into both the A \(\Pi\) and \(\Pi(0^+)\) states. Additionally, the value of \(r_c\) is allowed to vary in model 1, whereas it is fixed at the ab initio value\(^{41}\) of 2.7 Å in model 2. Figure 7 illustrates the quality of agreement of these two models with the five types of experimental data used in the analysis. Both models 1 and 2 give a significantly better overall quality of fit than the best of the previous models, as indicated by the RMSR values in Table 2 and the agreement seen in Figure 6.

Figure 8 compares the potential energy and transition moment functions of the two new models and deserves some comment. The main difference between these models is the use of an empirical linear function rather than a scaled ab initio transition moment function for the \(\Pi(0^+)\) state. In view of the rather different shapes of the \(\Pi(1)\) transition moment functions across the FC region for models 1 and 2, it is no surprise that the associated \(\Pi(1)\) state potentials differ significantly. It is surprising, however, that the potential energy and transition moment functions for the \(\Pi(1)\) state also change considerably. This result illustrates the high degree of correlation among the parameters defining the models and accounts for our inability to recommend one model over the other. We note that, except for the transition moment function for \(\Pi(0^+)\), the transition moment functions and potentials from model 1 closely resemble those from ref 43.

Prior to the present work, all experimental efforts have been directed at obtaining accurate values of \(\Gamma\) and \(\epsilon\) for the HI/\(\Pi\)\((\nu=0)\) photodissociation spectra. Both models 1 and 2 give

### Table 2: RMSR Values for Selected Models Considered in the Global Reanalysis of the HI/\(\Pi\)(\(\nu=0\)) Absorption Measurements and Branching Ratio Data from Ref 43 Including the New HI\((\nu=2, J=0)\) Branching Ratio Data

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<th></th>
<th>ref 43</th>
<th>model 1</th>
<th>model 2</th>
<th>model 2</th>
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<tr>
<td>RMSR, global</td>
<td>0.93</td>
<td>0.82</td>
<td>0.85</td>
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<tr>
<td>RMSR, ((r^0))</td>
<td>1.52</td>
<td>0.96</td>
<td>0.53</td>
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### Table 3: Parameters Defining the Potential Energy and Transition Moment Functions for HI and DI\(^a\)

<table>
<thead>
<tr>
<th>model</th>
<th>(A \Pi(1))</th>
<th>(a \Pi(0^+))</th>
<th>(a \Pi(1))</th>
<th>(t \Sigma^+(1))</th>
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<tr>
<td>(D/\text{cm}^{-1})</td>
<td>25778</td>
<td>25778</td>
<td>33381</td>
<td>25778</td>
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<td>(g_0)</td>
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<td>2</td>
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<tr>
<td>form</td>
<td>exp</td>
<td>exp</td>
<td>EMO</td>
<td>exp</td>
</tr>
<tr>
<td>(A/\text{cm}^{-1})</td>
<td>20873 (±110)</td>
<td>20384 (±68)</td>
<td>15188 (±290)</td>
<td>27690 (±200)</td>
</tr>
<tr>
<td>(\beta/\text{Å}^{-1})</td>
<td>2.304 (±0.044)</td>
<td>2.945 (±0.042)</td>
<td>2.965 (±0.79)</td>
<td>2.6</td>
</tr>
<tr>
<td>(\beta/\text{Å}^{-1})</td>
<td>-0.437 (±0.093)</td>
<td>-0.260 (±0.11)</td>
<td>2.495 (±0.11)</td>
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<tr>
<td>(c_0)</td>
<td>0.978 (±0.021)</td>
<td>0.4623 (±0.0064)</td>
<td>1.329 (±0.091)</td>
<td>1.0</td>
</tr>
<tr>
<td>(c_1)</td>
<td>-0.613 (±0.027)</td>
<td>0.4072 (±0.0068)</td>
<td>0.823 (±0.062)</td>
<td>1.0'</td>
</tr>
</tbody>
</table>

\(^a\) 95% confidence limit uncertainties are given in parentheses. The potential function exponent coefficients expansion variable is \(y_s(r)\), and the fit yields \(\Gamma(\text{DI}) = 1.09632 (±0.0039)\) for model 1 and 1/0.9365 (±0.0033) for model 2. See text or ref 43 for details. \(^b\) EMO potential form with fixed well depth \((\phi_0 = 600 \text{ cm}^{-1})\), and with \(r_c = 2.63892 (±0.032)\) Å for model 1 and \(r_c\) fixed at 2.7 Å for model 2. \(^c\) Transition moment defined as cubic spline through ab initio values from ref 41, multiplied by this scaling factor \(c_0\).
predictions that quantitatively agree with all previous experiments (Figure 7), but they yield significantly different potential energy curves and TMFs, even in the $V^0_{FC}$ region (Figure 8). Although the distinctly smaller value of RMSR($\Gamma$) given in Table 2 suggests that model 2 is preferred, relative to the uncertainties in our data, we cannot unequivocally recommend one model over the other. However, the total absorption cross sections and branching ratio predictions for models 1 and 2 for HI($v=0-4, J=0$) shown in Figure 9 reveal that photodissociation studies of vibrationally excited HI would differentiate them. In particular, measurement of the state selected absorption cross-sections as well as branching ratios should yield information capable of placing ever stricter constraints on the potential energy curves and transition moment functions of the excited states. This information also allows detailed comparison with improved ab initio calculations.

IV. Synthesis

Conventional spectroscopic methods are capable of probing the shape and nature of bound molecular electronic states in extraordinary detail. To take an example relevant to this work, consider the accuracy and precision to which the parameters defining the HI $X^1\Sigma^+(0^+)$ state are known. A recent spectroscopic study of HI aimed at determining the Born–Oppenheimer correction to the molecular Hamiltonian used 13 fitted parameters, which contain 4–10 significant figures, to characterize the $X$ state. In contrast, repulsive states have received much less attention because they are more difficult to study owing to experimental difficulties and their lack of sharp spectral features. The problem seems to be intractable when there are many excited states and the possibility of nonadiabatic effects. Here we have proposed another method—vibrationally mediated photolysis—to aid in untangling such states and their couplings. Measurements of the state-selected absorption cross-sections as well as branching ratios should yield information capable of placing ever stricter constraints on the potential energy curves and transition dipole moment functions of the excited states. This information also allows detailed comparison with improved ab initio calculations.

In the specific case of HI, we have demonstrated channel control over the resulting photofragments. We note that this method of passive control, where a specific vibrational eigenstate...
is prepared, is very different from that of coherent control.59,60 This work demonstrates that a proper choice of photolysis wavelength and initial HI rovibrational state allows over 80% of the photolytic iodine atoms to be prepared in the spin–orbit-excited level, whereas if HI is photolyzed from its ground vibrational level only about 50% of the iodine atoms can be prepared in the spin–orbit-excited level. The mechanism of this control is elucidated, and Figure 9 illustrates the importance of having a detailed understanding of the excited states, to predict how one can control this process.

The qualitative agreement of previous ab initio41 branching ratios and anisotropy parameters for HI(ν=2) with the present results attests to the quality of those calculations. This level of agreement is rather remarkable because relativistic corrections had to be introduced in obtaining the potential energy curves and transition moment functions. However, the present HI-(ν=2, J=0) photolysis data do differ systematically from those predictions, which suggests that further improvements in the ab initio calculations are needed.

The experimentally determined photofragment angular distributions strongly support the picture that HI photolysis proceeds without significant coupling between the different excited electronic states. Thus, we were encouraged to make a global reanalysis in the same spirit as Le Roy et al.43 using data for the photolysis of the HI vibrational ground state. We find from the global reanalysis that two empirical models are successfully able to reproduce all experimental data. Further experiments should be able to distinguish between these models and likely will lead to further improvements in the empirical fits. Indeed, Figure 9 illustrates many experiments that would be capable of differentiating between these models and elucidates the power of vibrationally mediated photolysis in providing more information about repulsive electronic states. Thus, for HI photolysis, despite so many years of study, the beat goes on.

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References and Notes