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High-resolution photoelectron spectroscopy of HI and DI: Experimental and theoretical analysis of the $A^2\Sigma^+$ ion system

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A combined high-resolution (6 meV) HeI photoelectron (PE) and ab initio theoretical study of the $A^2\Sigma^+$ ion system of HI and DI has been conducted to elucidate the origin of a peculiar “holelike” feature in the vibrational distribution found in the high-resolution (6 meV) threshold photoelectron (TPE) spectrum of HI. The PE and TPE spectra were found to yield essentially identical results. Ab initio potential energy curves for the low-lying cationic states of HI have been calculated for the first time with and without spin–orbit contributions included. It has been found that the diabatic $A^2\Sigma^+$ state of HI$^+$ is strongly predissociated due to spin–orbit coupling with the $4\Sigma^-$, $2\Sigma^-$, and $4\Pi$ repulsive states leading to a complex set of adiabatic curves. It is shown that the adiabatic $A^2\Sigma^+_{1/2}$ state is only slightly bound (by 260 cm$^{-1}$ after suitable adjustments of the positions of the various repulsive potentials relative to that of the A state are made based on observed atomic spectral data) and should support at most one vibrational level in both HI$^+$ and DI$^+$. However, using the complex rotational method, it was possible to calculate the energies, predissociation linewidths, and rotational constants of a number of nonstationary vibrational levels (or resonances) of the $A^2\Sigma^+_{1/2}$ state. Reasonably good agreement has been found between experiment and theory. The observed “hole” in the TPE and PE spectra is attributed to the fact that the stability of the $v^t=1$ and 2 levels is notably less than for $v^t=0$ in the $A^2\Sigma^+_{1/2}$ state of both HI$^+$ and DI$^+$. © 2003 American Institute of Physics. [DOI: 10.1063/1.1603735]

I. INTRODUCTION

Recently the results of a high-resolution (6 meV) threshold photoelectron spectroscopic (TPES) study of HI appeared in which a progression of fairly well resolved vibrational bands was found for the first time in the $A^2\Sigma^+$ system of HI$^+$. These findings were remarkable in three additional respects. First, the dominant vibrational spacings were found to be about half of what one would expect from a linear extrapolation of the vibrational constants of the $A^2\Sigma^+$ state of HCl$^+$ and HBr$^+$. Second, to account for the unexpected vibrational constant found within the $A^2\Sigma^+$ state of HI$^+$, an avoided crossing was invoked between the bound diabatic $A^2\Sigma^+_{1/2}$ state potential and the repulsive diabatic $4\Pi_{1/2}$ state potential, whose adiabatic asymptotic limit is $1^+(3P^0) + H(2S)$. This gave rise to two potentials with $\Omega=1/2$ designations. Third, to account for an apparent “missing” vibrational band in the $A^2\Sigma^+$ system, it was proposed that the $A^2\Sigma^+$ state was predissociated by the repulsive $4\Sigma^-$ state, whose asymptotic limit is $1^+(3P^0) + H(2S)$. This curve crossing was proposed to result in the extensive broadening of the “missing” vibrational band. These startling results prompted us to perform an equally high-resolution HeI photoelectron spectroscopic (PES) study of both HI and DI from which some new information is gained about the $A^2\Sigma^+$ band system of HI$^+$ and DI$^+$. This was coupled with a series of relativistic configuration interaction calculations to obtain the relevant potentials involving the $A^2\Sigma^+$ state of HI$^+$ and DI$^+$. Based on these new findings a comprehensive view of the $A^2\Sigma^+$ state potential in HI$^+$ and DI$^+$ is presented that explains the interesting and unusual spectroscopy of HI$^+$ and DI$^+$. 

II. EXPERIMENT

The photoelectron spectrometer used in these studies has been reported on in full detail elsewhere, so only a brief description will be given here. Helium radiation of high in-
tensity and narrow linewidth is produced in a microwave-powered electron cyclotron resonance source, and upon exiting the source is dispersed by a specially built monochromator that removes all resonance lines except the He I line of energy 21.2182 eV used in this study. In these experiments the photon beam intersected an effusive sample gas stream at 90° to each other at a point directly in front of the entrance to a lens system used to focus the kinetically energetic electrons onto the entrance slit of a double focusing hemispherical analyzer that was operated in a constant pass energy mode. The energy-analyzed electrons were detected using a microchannel plate system coupled to a phosphor screen and a charge-coupled device camera. The HI sample gas was commercially obtained. It was degassed at liquid nitrogen temperature to remove any hydrogen gas that accumulated in the lecture bottle due to decomposition of HI on the walls of the bottle. DI was prepared in situ on the gas inlet system of the apparatus by dehydrating a 53 wt% solution of DI in D₂O using solid P₂O₅. This solution was obtained from Aldrich Chemical Co., Inc., Milwaukee, WI.

III. COMPUTATIONAL METHOD

In the present theoretical treatment, the Λ–S contracted spin–orbit configuration interaction method is employed to obtain potential energy curves for the ground and lowest excited states of the HI⁺ ion. In this approach, a relatively small number of Λ–S states are calculated at first, while spin–orbit coupling between them is included at the next stage to obtain the final Ω states (for more details see Refs. 4 and 5). The core electrons of the I atom are described by a RECP given by LaJohn et al.⁷ and is described in more detail in Ref. 6. The (6s7p3d1f) fully uncontracted basis set employed for the I atom is adapted from the all-electron Gaussian Cartesian set of Glukhovtsev et al.⁷ and is described in more detail in Ref. 8. The atomic orbital basis for the hydrogen atom is the (7s3p)/[5s3p] set from Ref. 9 augmented by one d (1.00) polarization function. All calculations are carried out in the C₂v point group. The standard multi-reference single- and double-excitation CI approach (MRDCI) is used to obtain the Λ–S electronic energies. The calculations have been carried out employing the Table Direct-CI version¹⁰,¹¹ of the MRDCI package including configuration selection and perturbative corrections, with a selection threshold of $T = 0.05 \times 10^{-6} E_h$. From two to four lowest roots have been calculated for each of the doublet and quartet symmetries, and typical sizes of the generated CI spaces are from 1.8 to 2.7 $\times 10^6$, depending on symmetry, from which (18–32)$\times 10^9$ configurations have been selected. The importance of higher excitations has been assessed by applying the generalized multireference analogue of the Davidson correction to the perturbatively extrapolated $T = 0$ energies of each root.

The calculation of the vibrational levels of the $A^2\Sigma_{1/2}^+$ state is based on the ab initio Λ–S potential curves and spin–orbit coupling matrix elements. For this purpose, the complex rotation method, in conjunction with the Gauss–Hermite technique,¹² is applied to the Ω=1/2 components resulting from the lowest $X^2\Pi, A^2\Sigma^+, 4\Sigma^-, 2\Sigma^-$ and $^4\Pi \Lambda–S$ states of HI⁺ and DI⁺. A basis set composed of 250 complex rotated Hermite polynomials is employed with rotation angles being varied in a range from 2° to 5° in searching for the stabilized complex eigenvalues of the resonances. More details of the above-mentioned technique may be found in Ref. 12.

IV. EXPERIMENTAL RESULTS

The He I PE spectra of HI and DI covering the electronic band system of the $A^2\Sigma^+$ cationic state are shown in Fig. 1 at a resolution of 6 meV. In the upper panel the He I PE spectrum of HI is compared with the TPE spectrum of HI. In the lower panel the He I PE spectrum of DI is shown at two different resolutions.

![Figure 1](image-url)

**FIG. 1.** He I photoelectron spectra of HI and DI over the $A^2\Sigma^+$ band system of HI⁺ and DI⁺ at the resolutions indicated. In the upper panel the He I PE spectrum of HI is compared with the TPE spectrum of HI. In the lower panel the He I PE spectrum of DI is shown at two different resolutions.
the vibrational distribution, identified in our previous paper on the TPES of HI as the energy position of a “missing” vibrational band.\(^1\) Actually, this position corresponds to a slight peak within the “hole” best seen in the TPE spectrum. The \(v^+ = 3\) member in the identified progression is substantially shifted in energy from the \(v^+ = 1\) member. This energy spacing is also much larger than the spacings observed between all other members of the vibrational progression. This suggests that another member of the progression is also “missing.”

In the lower panel of Fig. 1 \(\text{He}\�\text{I} \) PE spectra of DI are shown at two different resolutions. These spectra show the same peculiar “hole” in the vibrational progression as found in the \(\text{He}\�\text{I} \) and TPE spectra of HI, but, except for the first peak, the vibrational bands of the observed progression are less well defined. This is most likely due to the smaller vibrational constant expected of the deuterated isotopomer, but the effect of enhanced predissociation coupling in DI\(^+\) cannot be ruled out at this point. The higher resolution \(\text{(4 meV) PE spectrum does show slightly sharper features, especially noticeable in the first vibrational peak. The vibrational progression ladder (Expt.) given in the lower panel of Fig. 1 was drawn to coincide with the positions of the peak maxima structure, except for the position of the second member that was placed at the bottom of the “hole” in the distribution by analogy with the HI PE and TPE spectra.

In an attempt to estimate the widths of the peak structure identified in Fig. 1 for both HI\(^+\) and DI\(^+\), we performed simple Franck–Condon simulation calculations using Morse potential functions for the ground and cationic states of HI/ DI. In order to simulate the overall spectra satisfactorily we had to use a composite potential for the cationic state made up of two simple Morse potentials, while for the ground state we used a single Morse potential. The generated Franck–Condon factors were then fitted by Gaussian functions yielding the peak widths [full width at half maximum (FWHM)] given in Table I together with the measured peak energy positions and energy separations.

V. THEORETICAL RESULTS

Potential energy curves calculated without including spin–orbit coupling are shown in Fig. 2. The \(X^2\Pi\ (\ldots\sigma^2\pi^2)\) ground state of HI\(^+\) results from the removal of the lone-pair \(\pi\) electron from the closed-shell \(1\Sigma^+\ (\ldots\sigma^2\pi^2)\) ground state of the neutral HI molecule. Since the \(\pi\) electrons are predominantly localized on the iodine atom and do not participate in bonding, the spectroscopic properties of the ground states in the neutral and cation systems are very similar. Most of the HI\(^+\) low-lying states originate either from the \(\pi\rightarrow\sigma^*\) (nonbonding to antibonding orbitals) electron excitation, as \(2\Sigma^+\), \(2\Delta\), and \(2\Sigma^+\ (\ldots\sigma^2\pi^2\sigma^*)\), or from \(\sigma\rightarrow\sigma^*\) (bonding to antibonding orbitals), as \(1\Pi\) and \(2\Pi\ (\ldots\sigma\pi\sigma\sigma^*)\). This explains their relatively high excitation energy (>4.5 eV) and repulsive character. The only exception is the \(A^2\Sigma^+\ (\ldots\sigma\pi\sigma)\) state, which arises from the bonding \(\sigma\) to the lone-pair \(\pi\) electron excitation. This requires not only less energy and the \(A^2\Sigma^+\) state is fairly strongly bound at the \(\Lambda\)–\(S\) level of treatment (by \(\sim 1.0\) eV) due to its convergence to the second \(H(2S)+1\Pi(1D)\) dissociation limit.

The final potential energy curves for \(\Omega\) states obtained including spin–orbit coupling are shown in Fig. 3. The \(X^2\Pi\) ground state is now split into the \(\Omega=1/2\) and \(3/2\) components, with the latter being the lower one. For the \(X^2\Pi_{3/2}\) state, \(\omega_e = 2160 \text{ cm}^{-1}\) and \(r_e = 1.625 \text{ \AA} \) are obtained, which is in good agreement with estimates of 2170 cm\(^{-1}\) and 1.620 \text{ \AA}, made on the basis of the experimental data for lighter isovalent systems,\(^13\) as well as with the earlier theoretical results.\(^14,15\) The calculated \(X^2\Pi\) splitting is 5276 cm\(^{-1}\), which also agrees well with the experimental value\(^13\) of 5400 cm\(^{-1}\). The \(X^2\Pi_{1/2}\) dissociation energy is computed to be 3.161 eV, which is 0.094 eV = 760 cm\(^{-1}\) lower than the experimental result,\(^13\) while the energy difference for the two lowest \(1^+\) \((1D)\) and \(1^+\) \((3P)\) dissociation limits is overestimated by approximately the same margin,\(^16\) 635 cm\(^{-1}\). Altogether, the above-mentioned spectroscopic data indicate reasonable accuracy for the present \textit{ab initio} treatment, although the slight overestimation of the \(\Delta E\) \((1D-3P)\) energy difference may be of critical importance for the \(A^2\Sigma^+\) properties.

As can be seen from Fig. 3, the character of the \(A^2\Sigma^+\) \(1/2\) state changes dramatically when spin–orbit interaction is included in the calculations. It is strongly predissociated due to spin–orbit coupling with the \(1/2\) components of the \(4\Sigma^-,\)
\(2\Sigma^-,\) and \(4\Pi\) states. The repulsive limb of the \(A^2\Sigma^+\) \(1/2\) state at long distances has predominantly \(4\Sigma^-\) character, but contributions from the other states are also significant in agreement with an earlier interpretation.\(^1\) The \(A^2\Sigma^+\) potential well is calculated to be only 134 cm\(^{-1}\) deep, which is not
levels (or resonances) of the $A^2Σ_{1/2}^+$ state of HI$^+$ and DI$^+$.

The calculated energy spacings for vibrational levels associated with the $A^2Σ_{1/2}^+$ state of HI$^+$ lie in the 340–560 cm$^{-1}$ range, while the $Γ_v^+$ values vary from 516 ($v^+=0$) to 976 cm$^{-1}$ ($v^+=5$), with both these results overestimating the experimental findings (see Fig. 1 and Table I). Based on the above-presented discussion of the $ab$ initio data, it is natural to suppose that the $A^2Σ_{1/2}^+$ state is calculated to lie too high with respect to the $4Σ^-$, $2Σ^-$, and $4Π$ states and this causes an error in the position of the corresponding avoided crossings. Therefore, we have carried out additional calculations of the $A^2Σ_{1/2}^+$ vibrational levels, shifting the $4Σ^-$, $2Σ^-$, and $4Π$ states upward by 800 cm$^{-1}$, the approximate error of the $ab$ initio results at the dissociation limit. The positions of the $X^2Π$ and $A^2Σ_{1/2}^+$ states have not been changed. Test calculations have also been made for a shift of 2000 cm$^{-1}$ for the same three states to further explore the possible influence of the above-mentioned effect on the $A^2Σ_{1/2}^+$ state properties. The calculated $E_v^+$, $ΔE_v^+$, $Γ_v^+$ and $B_v^+$ parameters for a shift of 800 cm$^{-1}$ (case A) and 2000 cm$^{-1}$ (case B) are given in Tables I and II for HI$^+$ and DI$^+$, respectively, and will be discussed in more detail in Sec. VI. Based on these results, vibrational progression ladders (Calc/case A) are given in the upper and lower panels of Fig. 1 by aligning the $v^+=0$ energy values for HI$^+$ and DI$^+$, respectively, with the experimental binding energies.

VI. DISCUSSION

From a comparison of the 800 cm$^{-1}$ shifted data (case A in Tables I and II) with the experimental measurements

![Graph](image-url)

**FIG. 3.** Potential energy curves for the lowest Ω states of HI$^+$ and DI$^+$ calculated with spin–orbit coupling: Ω=1/2—solid lines, 3/2—dashed lines, 5/2—a dotted line. The vertical dashed line indicates the equilibrium distance for the HI neutral system.

**TABLE I.** Measured peak energy positions ($E_v^+$, in eV), energy separations ($ΔE_v^+$, in cm$^{-1}$) and estimated peak widths (FWHM) ($Γ_v^+$, in cm$^{-1}$) derived from analysis of the HI He I PE spectrum given in Fig. 1 compared with the calculated energy positions ($E_v^+$), energy separations ($ΔE_v^+$), predissociation linewidths ($Γ_v^+$) and rotational constants ($B_v^+$) (in cm$^{-1}$) for the $A^2Σ_{1/2}^+$ state of HI$^+$.

<table>
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<th>Theory—Case B</th>
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*Values are given relative to the minimum of the diabatic potential curve of the $X^2Π$ state.
*Vertical shift of the $4Σ^-$, $2Σ^-$, and $4Π$ potentials by 800 cm$^{-1}$.
*Vertical shift of the $4Σ^-$, $2Σ^-$, and $4Π$ potentials by 2000 cm$^{-1}$.
*Uncertainty $±0.002$ eV.
*Uncertainty by as much as $±25\%$ for $v^+>1$; $±2\%$ for $v^+=0$.
*Evaluated $B_v^+$ value for the $v^+=0$ level of the $X^2Π$ state of HI$^+$ is 6.34 cm$^{-1}$.
Fig. 1 and Tables I and II), it can be seen that the vibrational spacings for the \( v^+ = 0 \to 5 \) levels of the \( ^2 \Sigma^+ \) state of HI and DI are in reasonably good agreement, while the predissociation linewidths are calculated to be broader (see Tables I and II) than found experimentally (see Fig. 1 and Tables I and II). However, we note that the estimates of the experimental peak widths (described earlier) may be in error by as much as \( \pm 25\% \) for \( v^+ \geq 1 \), whereas the widths of the \( v^+ = 0 \) peaks for HI and DI should be reasonably accurate \( \pm 2\% \). The calculated widths become more difficult to calculate accurately for the \( v^+ \geq 2 \) levels because of uncertainties in the locations and nonadiabatic couplings in this energy region. It is also not clear how well the complex rotational method performs for such large widths in a multichannel environment. The \( ^2 \Sigma^+ \) potential well is now 260 cm\(^{-1}\), which means that the lowest vibrational level lies just under the top of the barrier at \( r = 4.0 \) a.u. (see Table I). The experimental \( \Delta E_{v^+} \) (\( v^+ = 0 \to 1 \)) separation in the HI \( ^2 \Sigma^+ \) state is reproduced quite well, 329 versus 331 cm\(^{-1}\) (Expt.), but the \( \Gamma_0 \) linewidth (\( v^+ = 0 \)) is still overestimated, 389 versus 300 cm\(^{-1}\) (Expt.) (see Table I). This means that the tunneling probability for the \( v^+ = 0 \) level is calculated to be too high, indicating that the barrier to dissociation is lower and/or narrower than it should be. In addition, the apparent “hole” in the He I PE spectra of HI and DI (see Fig. 1), where the \( v^+ = 1 \) and 2 bands appear to be “missing,” still requires explanation. A strong drop in the \( B_{v^+} \) rotational constant value from \( v^+ = 0 \) to 1 may provide a possible basis for explaining this unusual spectral feature.

To further investigate this problem, we have carried out additional calculations with the \( ^4 \Sigma^- \), \(^2 \Sigma^- \), and \(^2 \Pi \) potentials shifted upward by 2000 cm\(^{-1}\). As one can see from Table I for HI\(^+\), in this case the \( v^+ = 0 \) level becomes more long-lived, 210 versus 300 cm\(^{-1}\) (Expt.). The most interesting result of these calculations is, however, the fact that the \( v^+ = 1 \) level has a very small rotational constant \( (B_1 = 2.02 \) cm\(^{-1}\) for HI\(^+\)), which is caused by its location close to the top of the barrier. This means that the \( v^+ = 1 \) vibrational wave function is localized quite far from the Franck-Condon (FC) region, the center of which is indicated by the vertical dashed line in Fig. 3. Calculation of FC factors from \textit{ab initio} data is complicated by the fact that the \(^2 \Sigma^+ \) vibrational states are resonances, and thus their wave functions have an imaginary component. If one simply uses the real parts in the calculations, it is found that the FC factors increase monotonically from \( v^+ = 0 \) to maximum values for \( v^+ = 5,6 \), as one would expect from the relative shapes of the HI ground state and HI\(^+\) excited state potentials. The imaginary parts of the \( v^+ = 1,2 \) levels are notably larger than that for the \( v^+ = 0 \) level, thus indicating a significantly higher degree of instability for the former. This fact seems to be quite important in understanding how the aforementioned hole in the spectrum comes about. Although the \( B_{v^+} \) rotational constants for the \( v^+ \geq 2 \) levels are also quite small, it is clear that the vibrational wave function overlap at the left wall of the \(^2 \Sigma^+ \) state increases fairly quickly with energy, which causes an increase in the PE spectral intensity with \( v^+ \) quantum number. This is especially obvious for the DI\(^+\) case (see the lower panel in Fig. 1), where the intensities for ionization to levels \( v^+ = 0 \) and 8 differ by almost a factor of 5, which is consistent with the computed FC factors discussed earlier.

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\(^a\)Values are given relative to the minimum of the diabatic potential curve of the \( X^2 \Pi \) state.

\(^b\)Vertical shift of the \(^2 \Sigma^+ \), \(^2 \Sigma^- \), and \(^2 \Pi \) potentials by 800 cm\(^{-1}\).

\(^c\)Vertical shift of the \(^2 \Sigma^+ \), \(^2 \Sigma^- \), and \(^2 \Pi \) potentials by 2000 cm\(^{-1}\).

\(^d\)Uncertainty \( \pm 0.002 \) eV.

\(^e\)Uncertainty by as much as \( \pm 25\% \) for \( v^+ \geq 1 \); \( \pm 2\% \) for \( v^+ = 0 \).

\(^f\)Evaluated \( B_{v^+} \) value for the \( v^+ = 0 \) level of the \( X^2 \Pi \) state of DI\(^+\) is 3.21 cm\(^{-1}\).
VII. SUMMARY

High-resolution HeI photoelectron spectra of HI and DI have been measured and found to be in good agreement with the TPES data obtained earlier. Vibrational levels of the \( A^2\Sigma^+ \) state are strongly predissociated and both the HeI PE and TPE spectra show a peculiar “hole” at energies where the \( v^+ = 1 \) and 2 levels should be located. Spin–orbit CI calculations of the excited states of the HI and DI cations have been carried out for the first time and the complex rotation method is employed on this basis to obtain energies and predissociation linewidths of the vibrational levels of the \( A^2\Sigma^+_{1/2} \) state. The calculated and experimental data are shown to be in reasonably good agreement with each other and the present theoretical analysis, in particular with the slightly adjusted data, provides an explanation of the main features of the observed spectra. Based on the shallowness of the depth of the adiabatic potential energy curve for the \( A^2\Sigma^+_{1/2} \) state of HI\(^+\) and DI\(^+\) and the calculated predissociation linewidths of the associated vibrational levels (or resonances), it is unlikely that fluorescence would be observed from this state, and to our knowledge, none has been reported to date.

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