

Observation of vibrational excitation in photoelectron spectroscopy of $\text{HI}^+ \ ^2\Pi$

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Using photoelectron spectroscopy in combination with synchrotron radiation, we have observed previously inaccessible vibrational excitation of $\text{HI}^+ \ X \ ^2\Pi_{3/2}$, $X \ ^2\Pi_{1/2}$ final ionic states. The vibrational enhancement is shown to be caused by strongly predissociating autoionization resonances converging to $\text{HI}^+ \ A \ ^2\Sigma^+$. Molecular vibrational constants are extracted from the photoelectron spectra obtained at different excitation energies.

1. Introduction

Usually, when an electron from a non-bonding orbital is removed in the photoionization of a molecule, only slight vibrational excitation occurs for the direct ionization channel. Nevertheless, the influence of autoionization resonances involving electronic excitation from other (bonding or anti-bonding) orbitals can cause a significant change in the vibrational distribution due to the different Franck-Condon overlap via the resonant state. If, however, such excited states predissociate strongly, distinct vibrational structure in the photoexcitation spectra may be washed out and be unobservable due to severe broadening.

The vacuum ultraviolet photoionization of hydrogen iodide involving the outer electron orbitals represents such a case. The HI^+ ion can be left in its spin-orbit split ground state, $\text{HI}^+ \ X \ ^2\Pi_{3/2}$ and $X \ ^2\Pi_{1/2}$, in the vibrational levels ($v' = 0$) and ($v' = 1$) with the latter populated more than thirty times less, as seen from a photoelectron spectrum with HeI resonance radiation [1]. Apparently, due to the non-bonding character of the $5p\pi$ orbital involved, the internuclear separation does not increase much upon ionization and levels with $v' > 1$

lie outside the Franck-Condon region. In addition, the first excited ionic state $A \ ^2\Sigma^+_{1/2}$ (corresponding to the removal of an electron from a bonding σ orbital) is observed as a broad feature with no distinct vibrational structure in contrast to the lighter hydrogen halides HBr and HCl where several vibrational levels are seen in the corresponding photoelectron peaks [2]. Price and co-workers [2] concluded from their HeI spectra that for HI, unlike HCl and HBr, due to the position of the crossing of the $^2\Sigma^+$ potential curve with the $^4\Pi$ repulsive curve, all vibrational levels of $^2\Sigma^+$ are predissociated (see fig. 1). Consistent with this picture, autoionization studies of the hydrogen halides using photoabsorption spectroscopy [3] and photoionization mass spectrometry [4] in the energy region between the ground state and the first excited state of the ion have shown that, in contrast to HCl and HBr, HI does not yield any distinct vibrational progressions of Rydberg series converging to the $^2\Sigma^+$ state. For HI, only a broad structureless peak at around 100 nm appears in the absorption spectra indicating predissociation of the highly excited autoionizing states (labelled Ry in fig. 1). Predissociation of the upper state is also most likely the reason why the $A \ ^2\Sigma^+ - X \ ^2\Pi$ ionic emission bands were not observed in the case of HI [5].

Therefore, in contrast to the lighter hydrogen halide ions, spectroscopic information is scarce for HI^+

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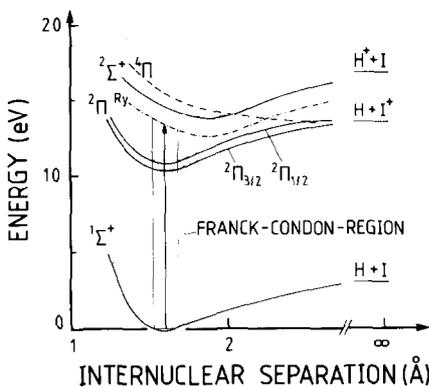


Fig. 1. Potential curves of HI adapted from ref. [2]. Indicated by the arrow is the excitation of Rydberg states (Ry) converging to the $A^2\Sigma^+$ ion state.

[6]. In particular, as far as vibrational excitation is concerned, up to now only the first intervals $\Delta G_{1/2}$ for $HI^+ 2\Pi$ could be obtained experimentally [1,7]. Carlson and co-workers [8] have observed that in the energy region below the $HI^+ 2\Pi_{1/2}(v' = 1)$ limit, the population of the $2\Pi_{3/2}(v' = 1)$ final ionic states is drastically increased due to the influence of spin-orbit autoionization resonances. Recently, at much higher excitation energy, Baltzer et al. [9] have reported vibrational structure in proton emission spectra related to the fragmentation of the $HI^+ B^2\Sigma_{1/2}$ state. However, distinct vibrational excitation higher than $v' = 1$ has previously *not* been observed for $HI^+ X^2\Pi$ and $A^2\Sigma^+$ and related Rydberg states in photoelectron spectroscopy, photoemission spectroscopy and photoabsorption/photoionization spectroscopy, as well. Consequently, no spectroscopic information exists concerning the vibrational energy levels $v' > 1$ for any of these states. Nevertheless, by using photoelectron spectroscopy in combination with a source of variable photon energy, high vibrational excitation of the final ionic 2Π states of HI^+ can be observed although the resonances are strongly predissociated. In this Letter, we report such spectra and discuss the cause of vibrational excitation and the extraction of vibrational constants.

2. Experimental

With our apparatus at BESSY at the 6.5 m nor-

mal-incidence monochromator (see ref. [10] for a detailed description), we have examined the photoemission of electrons at the magic angle ($\Theta_m = 54.7^\circ$) from an effusive molecular beam of HI in the wavelength region from 120 to 60 nm. The HI gas (better than 98% purity, supplied by Merck-Schuchardt) was used without further purification. Traces of impurities other than H_2 were not observed in the photoelectron spectra. A cold trap filled with liquid nitrogen was added to freeze the HI molecules after crossing the ionization region; the background pressure inside the vacuum chamber was less than 9×10^{-5} mbar. The photoelectrons produced were analyzed angle-resolved by a simulated hemispherical spectrometer [11,12] and detected by a channeltron. The data acquisition was computer controlled using a programmable power supply for the spectrometer ramp voltage. Relative ramp voltages could be determined with an accuracy of 0.3 mV or better, as was checked independently. The decrease in radiation intensity, while recording the photoelectron spectra, was corrected for by normalizing to the beam current of the electrons stored in the storage ring which was monitored simultaneously. When necessary, a characteristic background signal of low-energy electrons was subtracted from the spectra. The entrance and exit slits of the spectrometer were reduced so that an energy resolution of $\Delta E = 80$ meV could be achieved (at a wavelength resolution of $\Delta\lambda = 0.17$ nm). (Initially, data were taken at lower resolution as reported in a preliminary account [13].)

3. Results and discussion

A typical photoelectron spectrum is shown in fig. 2. The outer electronic configuration of the ground state of HI is $(5s\sigma)^2(5p\sigma)^2(5p\pi)^4$. Photoionization to $HI^+ X^2\Pi$, corresponds to the removal of one of the four outer lone-pair π electrons localized at the I atom. This gives rise to the intense peaks with $v' = 0$. In addition, sequences of weaker photoelectron peaks have been observed. They are assigned to vibrationally excited levels of the two spin-orbit states with the higher vibrational peaks of $X^2\Pi_{3/2}$ "buried" under those of $X^2\Pi_{1/2}$. Substantial vibrational excitation was detected *only* in the region from the ion-

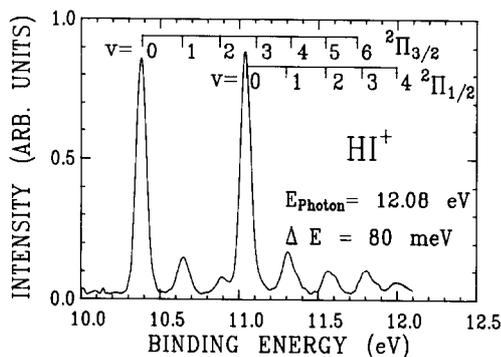


Fig. 2. Photoelectron spectrum for $\text{HI}^+ X^2\Pi$, final ionic states obtained at $\lambda = 102.6$ nm. The data (typical relative error: 10%) are corrected for the spectrometer transmission characteristics.

ization thresholds up to excitation energies of about 13.5–13.6 eV. On the other hand, at photon energies above 13.9 eV (in the wavelength range of 89 to 60 nm), levels with $v' > 1$ were not observed in the spectra and the relative intensities of the $v' = 1$ levels were very low, in agreement with the HeI spectrum [1]. In the region from 91.8 to 90.0 nm, the intensity of levels with $v' > 1$ decreased strongly. At 91.0 nm, vibrationally excited levels up to $X^2\Pi_{1/2}(v' = 10)$ were detected in the photoelectron spectrum.

Fig. 3 gives a summary of some representative data obtained in the wavelength range from $\lambda = 112.5$ to 90.0 nm and illustrates the variation of the spectra as a function of excitation energy. The spectra exhibit weak secondary maxima in the vibrational intensity distribution (as a function of photoelectron energy) as expected qualitatively from the influence of vibrationally excited autoionization resonances [14]. The level $^2\Pi_{3/2}(v' = 2)$ is clearly resolved and relatively intense in the wavelength region 112.5–109 nm. On the other hand, it is fairly weak in comparison to the vibrationally excited levels of the $^2\Pi_{1/2}$ state at shorter wavelengths indicating that the $^2\Pi_{3/2}(v' > 1)$ series is weaker than $^2\Pi_{1/2}(v' > 1)$. In the region of spin-orbit autoionization between the $\text{HI}^+ ^2\Pi_{3/2}$ and $^2\Pi_{1/2}(v' = 0, 1)$ thresholds, sharp structures have been observed in the excitation spectra [8,15]. In contrast to this, the partial [15] and total cross-section [3,4] results are dominated by strong broadening in the energy region above the $^2\Pi_{1/2}$ limits (corresponding to the energy region of fig. 3).

These broad resonances can be assigned to Ryd-

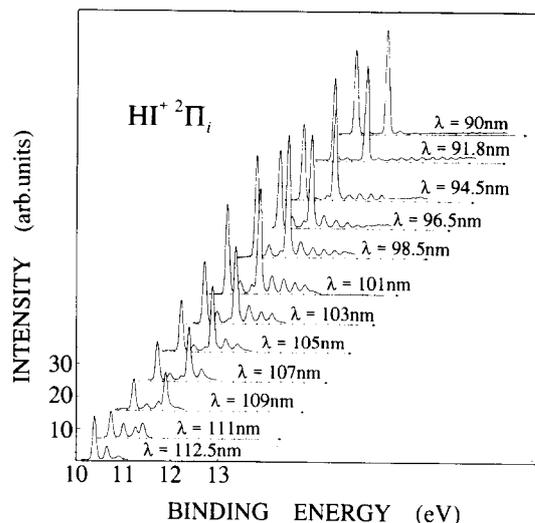


Fig. 3. Photoelectron spectra of HI in the wavelength region of 112 to 90 nm (not corrected for spectrometer transmission characteristics). Energy resolution: 80 meV; optical resolution: 0.17 nm.

berg states with a $(5s\sigma)^2(5p\sigma)(5p\pi)^4 A^2\Sigma^+$ core (see fig. 1), which give rise to electronic autoionization by interaction with the $^2\Pi_i$ continua. This assignment is based on analogies and is strongly supported by observation of corresponding processes in the photoionization spectra of HCl, DCl, HBr and DBr [3,4,16]. For these molecules, the structures are much sharper and distinct vibrational progressions are present. In particular, Cafolla et al. [16] have reported the corresponding data to fig. 3 for photoionization of HCl. The $\text{HI}^+ A^2\Sigma^+$ state can dissociate by spin-orbit predissociation due to a curve crossing with the $(5s\sigma)^2(5p\sigma)(5p\pi)^3(6s\sigma) ^4\Pi$ repulsive state, as was first inferred from HeI photoelectron spectra by Lempka et al. [2].

Likewise, the corresponding Rydberg states can dissociate and there is competition between autoionization and predissociation [17–19]. Due to the position of the curve crossing, the dissociation process is weak for HCl and dominant for HI where the lifetime is shorter than a vibrational period. Even though the Rydberg states dissociate to $\text{H} + \text{I}^*$, they can cause a strong enhancement of the ionization cross section.

Since an electron from a bonding orbital is excited, the Franck-Condon overlap is altered for the resonant contribution (see fig. 1). (A rigorous the-

oretical treatment of vibrational overlap in electronic autoionization was given by Smith [20].) Due to the presence of the intermediate state, high vibrational levels of the final ionic $X^2\Pi_i$ states can be populated. The intensities of the different levels are essentially determined by the product of the Franck-Condon factors linking the ground state with the autoionizing state and the autoionizing state with the ionic state. Since the final ionic states are stable, the corresponding photoelectron peaks are sharp although the resonances are predissociated and the related features in the photoionization spectra are strongly broadened.

The lowest series limit for the Rydberg states is the adiabatic ionization potential of $HI^+ A^2\Sigma^+$ at 13.85 eV [2]. Therefore, it has to be explained why the autoionization features causing vibrational excitation already vanish at $h\nu \approx 13.5\text{--}13.6$ eV. In principle, there are several decay processes for the resonances HI^* which can compete with molecular-ion formation: fluorescence, negative-ion formation and neutral and ionic dissociation. Fluorescence should be weak because of the short lifetimes of the resonances. The threshold for negative-ion formation should be at around 13.6 eV as can be estimated from the ionization potential of H, the electron affinity of I and the dissociation energy of HI. However, the respective thresholds for HBr and HCl (at 14.0 and 14.4 eV) are not associated with a disappearance of the corresponding resonance structures for these molecules and, furthermore, I^- formation was not observed in contrast to Cl^- formation in a recent experiment [21]. Thus, coupling to the ionic dissociation process $HI^* \rightarrow H + I^+ + e^-$ remains. Indeed, the threshold for this process occurs at 13.5 eV [7], as can also be inferred from the dissociation energy of HI, $D_0 = 3.054$ eV [6], and the $I^+ (^3P_2)$ -ionization limit (10.454 eV) [22]. This is also the dissociation limit of the $^2\Pi_i$ molecular-ion states. (The limit lies lower than the $A^2\Sigma^+$ threshold only for HI, and not for HBr and HCl.) Consequently, the resonances are only present as long as neutral dissociation competes with molecular ionization, and they disappear with the onset of ionic dissociation which then dominates and causes production of I^+ .

4. Determination of vibrational constants

Photoelectron spectra of the type presented in figs. 2 and 3 can be used to extract vibrational frequencies associated with the $HI^+ ^2\Pi_i$ states. In order to obtain the energetic positions of the vibrational levels, Gauss profiles were fitted to the various peaks in thirty different spectra. To obtain the positions for the levels $^2\Pi_{3/2}(v' = 2\text{--}4)$, the fitted $^2\Pi_{1/2}(v' = 0, 1)$ peaks were subtracted from the spectra. For the evaluation of the $^2\Pi_{1/2}$ series, it was assumed that perturbations caused by the underlying $^2\Pi_{3/2}$ series are negligible, since this series is weaker and since the levels $^2\Pi_{3/2}(v' = 4, 5, 6)$ almost coincide with $^2\Pi_{1/2}(v' = 1, 2, 3)$ (see fig. 2). By applying the fitting process to all available spectra, we obtained several values for the levels $^2\Pi_{3/2}(v' = 0\text{--}4)$ and $^2\Pi_{1/2}(v' = 0\text{--}9)$. Using these data as input, we then determined the vibrational frequencies ω_e and anharmonicity constants $\omega_e x_e$ independently for the two spin-orbit states by means of a least-squares fitting procedure. The results are given in table 1 together with the value determined for the spin-orbit splitting A_0 of the ($v' = 0$) levels. Alternatively, the results may be converted to common vibrational constants for $HI^+ ^2\Pi$ and a spin-orbit constant $A(v)$ with anharmonic terms according to

$$A(v) = A_e - \alpha_A(v + 1/2) + \beta_A(v + 1/2)^2.$$

These constants are also listed in table 1 although the small vibrational dependence of $A(v)$ is determined with relatively large error. The values for the first intervals, $\Delta G_{1/2}(^2\Pi_{3/2}) = 2139 \pm 19 \text{ cm}^{-1}$ and $\Delta G_{1/2}(^2\Pi_{1/2}) = 2148 \pm 9 \text{ cm}^{-1}$, as well as those for the frequencies ω_e and the spin-orbit splitting A_0 ,

Table 1
Constants for vibrational frequencies, anharmonicities and spin-orbit splitting for $HI^+ ^2\Pi_i$ final ionic states in units of cm^{-1} . As described in the text, two equivalent sets of constants (I, II) are listed

I	II
$\omega_e(^2\Pi_{3/2}) = 2256.1 \pm 3.4$	$\omega_e(^2\Pi) = 2252.7 \pm 2.2$
$\omega_e x_e(^2\Pi_{3/2}) = 58.6 \pm 9.6$	$\omega_e x_e(^2\Pi) = 54.7 \pm 5.2$
$\omega_e(^2\Pi_{1/2}) = 2249.2 \pm 2.9$	$A_e = -5358.1 \pm 4.3$
$\omega_e x_e(^2\Pi_{1/2}) = 50.8 \pm 4.1$	$\alpha_A = -6.9 \pm 4.4$
$A_0 = -5356.6 \pm 5.5$	$\beta_A = -8 \pm 10$

are comparable to previous estimates and results with lower precision [1,2,6,7]. By assuming constancy of $x_e\mu^{1/2}$ (with μ =reduced mass) and comparing with the values of $\omega_e x_e$ for the lighter hydrogen halides [6] or by taking the dissociation energy of $\text{HI}^+ \ ^2\Pi_{3/2}$ ($D_0=3.12$ eV) [6] into account, we can estimate a value of the order of 45 cm^{-1} for $\omega_e x_e$. The anharmonicities found here are somewhat larger, in particular for the $\ ^2\Pi_{3/2}$ state. This cannot be explained by insufficient separation of the $\ ^2\Pi_{3/2}$ series from the $\ ^2\Pi_{1/2}$ series. Our first results obtained at a resolution of $\Delta E=130$ meV showed the same trend but the $\ ^2\Pi_{3/2}(v'=2)$ level was only marginally resolved as a shoulder in the wing of the $\text{HI}^+ \ ^2\Pi_{1/2}(v'=0)$ peak [13]. Therefore, we repeated the measurements at $\Delta E=80$ meV paying special attention to record sufficient data in the wavelength region of $\lambda=112\text{--}109$ nm where the $\ ^2\Pi_{3/2}(v'=2)$ peaks are fairly intense and clearly resolved.

The spin-orbit splitting of the $\text{HI}^+ \ ^2\Pi$ potential curves is substantial and $\omega_e x_e$ and ω_e might be expected to be slightly different for the two sublevels. Furthermore, the data evaluation was based on the assumption of identical rotational envelopes for both fine-structure levels. They may actually be notably different due to differences in rotational coupling. In order to determine the spectroscopic constants with higher precision, experimental methods with very high resolution are needed. Infrared laser-magnetic-resonance (LMR) spectroscopy which was employed for DBr^+ [23] or zero-energy-kinetic-energy (ZEKE) photoelectron spectroscopy [24] might prove to be feasible techniques for such studies.

5. Conclusions

Our measurements have demonstrated that photoelectron spectroscopy together with tunable VUV radiation can reveal vibrational excitation, although in related photoabsorption experiments vibrational progressions cannot be discerned due to predissociation of the resonances involved. Vibrationally excited states of $\text{HI}^+ \ ^2\Pi$ could be detected from the respective threshold up to the ionic dissociation limit. The results were utilized to obtain information on

vibrational constants which was previously unavailable.

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