

Mechanism of the coherent control of the photoionization and photodissociation of HI and DI

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Abstract

Two experiments were performed to determine the mechanism responsible for the phase lag between the HI⁺ and I⁺ signals observed by Zhu et al. (Science, 270 (1995) 77) in the one- versus three-photon coherent control of the decay of excited HI and DI. In the first experiment a pulse of 266 nm radiation was introduced before the UV and VUV control pulses. It was observed in this case that the modulation amplitudes of the I⁺ signal decreased slightly, whereas the modulation depths decreased by a factor of two. This experiment rules out the possibility that modulation of I⁺ is caused by coherent control of the ionization of I atoms generated by two-photon photodissociation of the parent molecule. In the second experiment a fluorescence excitation spectrum produced by a single VUV photon was recorded and is attributed to emission from the atomic iodine product. Both experiments support our original interpretation of the phase lag arising from coherent control of the branching ratio for autoionization versus predissociation of the excited parent molecule. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

A fundamental principle of quantum mechanics is that the probability of a transition from state $|a\rangle$ to state $|b\rangle$ is equal to the square of the sum of the probability amplitudes for all independent paths connecting the two states [1]. It follows that by altering the relative phases of a set of competing paths it is possible to control the transition probability. This result applies regardless of whether $|b\rangle$ is a discrete or a continuum state. An interesting case arises when $|b\rangle$ is a degenerate superposition of continuum states that correlate asymptotically to different reaction

products. A decade ago Brumer and Shapiro [2] showed theoretically that by adjusting the phases of the different paths it is possible to modify the coefficients of the superposition state and thereby to control the branching ratio of the reaction products.

In an attempt to test the Brumer–Shapiro theory, Zhu et al. [3] irradiated a molecular beam of HI molecules with a laser beam at 355 nm and its third harmonic. Ionic products HI⁺ and I⁺ were detected with a mass spectrometer. As the relative phase of the two laser beams was increased, the two ion signals were modulated with a periodicity that matched that of the laser phase difference. Moreover, the modulated ion signals were out of phase with respect to each other, with the HI⁺ signal lagging

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the I^+ signal by $\sim 150^\circ$. These results were interpreted as follows. A superposition state is populated by absorption of three UV photons of frequency ω_1 and one VUV photon of frequency $\omega_3 = 3\omega_1$. The two absorption processes constitute the two paths of the Brumer–Shapiro theory, and variation of the laser phase difference produces a modulation of the coefficients of the resulting superposition state. The excited molecule either autoionizes to produce HI^+ or predissociates to form neutral products $H + I^*$, where I^* is electronically excited. The excited atom subsequently absorbs one or two ω_1 photons to produce I^+ . We refer to this scenario as ‘Mechanism 1’.

According to Mechanism 1, the phase lag between the two product signals can be explained as follows. The probability of forming product S is given by [4]

$$P^S = P_1^S + P_3^S + 2P_{13}^S \cos(\Delta\phi + \delta_{13}^S), \quad (1)$$

where P_3^S and P_1^S are the probabilities associated with the one- and three-photon paths, respectively, P_{13}^S is an intensity-dependent cross term, $\Delta\phi$ is the relative phase of the lasers, and δ_{13}^S is a channel-dependent phase shift which arises, in part, from the fact that the wave function of the continuum state is complex. The phase lag $\Delta\delta$ between the two signals equals $\delta_{13}^{HI^+} - \delta_{13}^{I^+}$, and arises from the different phases of the outgoing waves in the two reaction channels produced from a degenerate excited state of the parent molecule [5,6].

More recently we measured the wavelength dependence of $\Delta\delta$, and showed how a resonant state embedded in the two continua affects the phase lag [7]. The essential features of Mechanism 1 remained unchanged by this further study. There is, however, an alternate possible interpretation of our data, referred to as ‘Mechanism 2’ which, if correct, would profoundly alter the meaning of our observations. According to this mechanism, HI^+ is produced as in Mechanism 1. Atomic iodine, however, is formed by two-photon ($2\omega_1$) excitation of HI, followed by (pre-)dissociation to yield ground state $I(^2P_{3/2})$ or $I(^2P_{1/2})$ atoms. The I fragment subsequently absorbs both ω_3 and $3\omega_1$ to produce the detected I^+ . Modulation of the I^+ signal results from interference between this second pair of paths. The phase lag in this case arises from two independent reactions (ioni-

zation of HI and ionization of I), and the fact that HI happens to be the precursor of I is only incidental. According to Mechanism 2, the observation of a phase lag does not imply control of the branching ratio of a reaction, inasmuch as HI^+ and I^+ are produced independently. Although various indirect arguments were presented in the original paper [3] supporting Mechanism 1 (such as, for example, the absence of atomic I resonances and the presence of molecular HI resonances in the I^+ spectrum), a direct test of Mechanism 2 is clearly desirable.

The basis for suspecting that Mechanism 2 might contribute to the observed modulation is seen in the UV multiphoton ionization (MPI) spectra of HI and DI, displayed in Fig. 1. Clearly visible in the HI^+ and DI^+ scans are the $2 + 1$ (or $2 + 2$ for $\lambda > 358$ nm) resonance-enhanced MPI spectra of the $b^3\Pi_1$ and $b^3\Pi_2$ Rydberg states of HI and DI. Potential

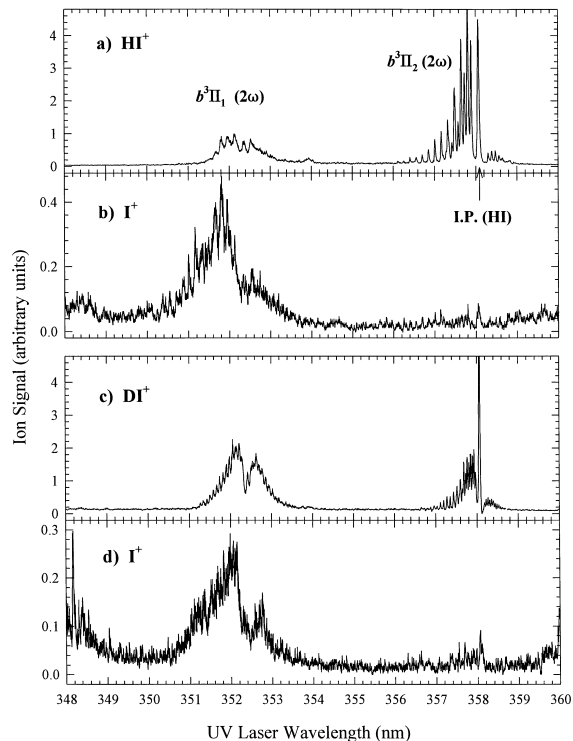


Fig. 1. Multiphoton ionization spectra of HI and DI. The upper two panels correspond to (a) HI^+ produced by multiphoton ionization of HI, (b) I^+ produced by two-photon dissociation of HI followed by multiphoton ionization of I. The lower two panels are the corresponding spectra for DI. The arrow indicates the three-photon ionization threshold of HI.

energy curves for these states are shown in fig. 2 of Ref. [3]. The corresponding I^+ spectra show that these states are strongly predissociated. The phase control experiments were performed at wavelengths lying between these two features (353.5–356.0 nm). The hypothesis of Mechanism 2 is that predissociation of the $b^3\Pi_{1,2}$ states, or direct photodissociation at intermediate wavelengths, produces I atoms that are ionized by $\omega_3/3\omega_1$ excitation. This possibility is illustrated more clearly in Figs. 2 and 3, where the long wavelength tail of the $b^3\Pi_1$ feature is shown on an expanded scale. Clearly visible in these spectra are the $5s\sigma$ resonances excited by $3\omega_1$ photons and the O-branch of the two-photon $b^3\Pi_1 \leftarrow \leftarrow X^1\Sigma^+$ transition. In the actual control experiment, where the UV intensity was lower, the relative contribution of the two-photon features was probably greater. Examination of the blue tail of the $b^3\Pi_2 \leftarrow \leftarrow X^1\Sigma^+$ transition shows similar evidence of two-photon generation of I atoms. It is therefore important to deter-

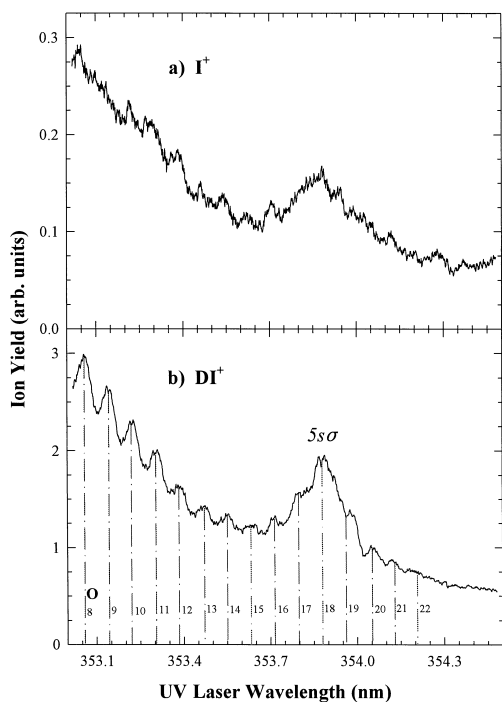


Fig. 2. Red edge of the MPI spectrum of the $b^3\Pi_2$ state of DI. The two panels show (a) the I^+ signal produced by two-photon dissociation of DI followed by multiphoton ionization of I, and (b) the parent molecular ion signal. Shown in the bottom panel are assignments of the two-photon O-branch of the $b^3\Pi_2$ state, and the three-photon $5s\sigma$ resonance of DI.

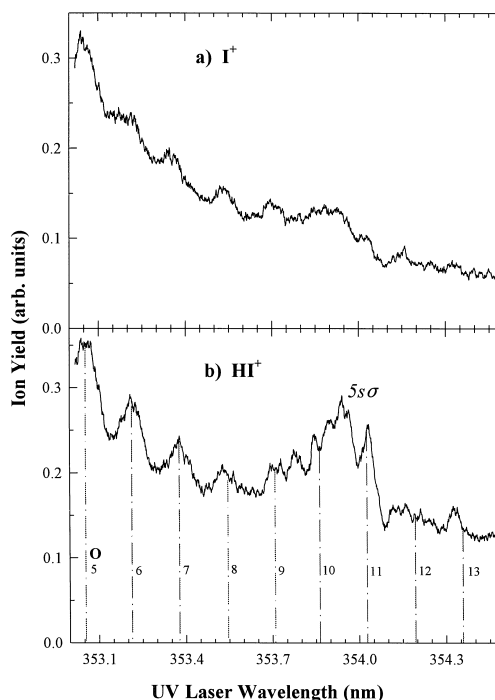


Fig. 3. Same as Fig. 2, only for HI.

mine whether I atoms produced by this route contribute to the modulated signal via Mechanism 2.

In the present study two experiments were performed to test the relative importance of Mechanisms 1 and 2. In the first experiment ground state I atoms were generated by a 266 nm laser pulse which preceded the UV/VUV laser pulses normally used in the control experiments. The logic behind this experiment is that if ground state I atoms are the source of the modulated I^+ signal (Mechanism 2), then photodissociation of HI by the first laser pulse would increase the modulation amplitude, whereas if I^* produced by the control pulses is responsible for the modulated signal (Mechanism 1), the photodissociation of HI by the first pulse would reduce the modulation amplitude. In the second experiment we measured the fluorescence excitation spectrum of HI by a single ω_3 photon to find direct evidence for the production of I^* .

2. Experimental

The method and apparatus used in the coherent control experiments of HI have been described in

detail previously [3]. Briefly, the one- and three-photon excitation sources were generated by focusing the UV output from a dye laser into a tripling cell containing Xe gas. Because of the conditions of third harmonic generation [8], the VUV beam thus generated exited the tripling cell with a well defined phase relative to the UV beam. This relative phase was varied in a controllable manner by passing the co-propagating laser beams through a chamber containing a variable pressure of a gas with a refraction index that differs significantly at the UV and VUV wavelengths [9]. In these experiments, H₂ gas served as the ‘phase-tuning’ medium. The tuning chamber held two spherical mirrors which were used to obtain a mutual focus for the UV and VUV beams in the main reaction chamber. The HI molecules were introduced perpendicular to the UV/VUV beams by an unskipped pulsed valve, and the ionic products were detected by a time-of-flight (TOF) mass spectrometer.

In the first experiment a ‘prepulse’ was used to photodissociate some of the HI molecules, producing ground state I atoms with comparable populations of the I(²P_{3/2}) and I(²P_{1/2}) spin-orbit states [10]. The dissociating pulse was the fourth harmonic (266 nm) of a Nd:YAG laser (Quantel 580, oscillator only, ~20 mJ/pulse, 10 ns pulse width). The control pulses were produced by a XeCl excimer-pumped dye laser (Lambda Physik Lextra 50/ScanMate II using DMQ dye, 4 mJ/pulse, 14 ns pulse width). The dissociation pulse preceded the control pulses by ~150 ns. The 266 nm laser beam was loosely focused with a 500 mm S1-UV lens, intersected with the control laser at a 45° angle, and was detected with a fast photodiode. Some of the I atoms produced by the 266 nm laser were ionized by the same laser pulse, and another fraction of these atoms were ionized later by the control laser. The delay between the two pulses completely separated the two I⁺ signals.

The experiment was carried out in two steps. First, the 266 nm laser was blocked, and a scan of the modulated HI⁺ and I⁺ signals was recorded. Immediately afterwards, the scan was repeated with the dissociation pulse preceding the control pulse.

The second experiment was conducted in a cubical Monel cell (10 cm inner width) equipped with 2.5 cm diameter LiF windows on four of its faces.

The cell was filled with a static pressure of approximately 0.1 Torr of HI gas. The UV pulse produced by the same dye laser used in the control experiments was focused by an S1-UV lens ($f = 7.5$ cm, $d = 2.5$ cm) into a tripling cell containing ~15 Torr of Xe gas. The resultant VUV light was then focused by a 2.5 cm diameter MgF₂ lens into the center of the reaction cell. The focal length of this lens was 125 mm at 355 nm and approx. 105 mm at 118 nm. At the opposite cell face, the UV pulse was monitored by a fast photodiode. The difference in focal length at the UV and VUV wavelengths allowed for the selective detection of fluorescence from species produced by the VUV photon only. Argon purge gas was flowed in the region between this lens and the window mounted on the cell. The fluorescence was collected at 90° by a MgF₂ lens ($f = 7.5$ cm, $d = 2.5$ cm) and was detected by a solar blind photomultiplier tube (PMT, EMR model 541G-09-17-03900). No fluorescence was detected in the absence of the purge gas. The PMT and photodiode signals were averaged by a dual channel boxcar integrator and were stored in a computer. Attempts to disperse the fluorescence with a monochromator failed because of insufficient signal.

In a separate measurement, the one-photon VUV ionization spectrum was recorded using the molecular beam TOF apparatus. The VUV pulse was produced as in the fluorescence experiment, and was crossed at a 45° angle by a UV probe laser pulse. The probe laser was the third harmonic (355 nm) of a Nd:YAG laser. It was loosely focused by a 100 mm S1-UV lens at right angles to the pulsed molecular beam. The excitation and detection beams were temporally and spatially overlapped, so that the ion signal produced by the probe laser alone was significantly enhanced in the presence of the VUV beam.

3. Results and discussion

3.1. Control / pre-pulse experiment

In Fig. 4, an example of the control scans of HI⁺ and I⁺ with and without the preceding 266 nm laser pulse is shown. The modulations of the HI⁺ and I⁺ signals were fitted to the function

$$F(\theta) = A + B \cos \theta, \quad (2)$$

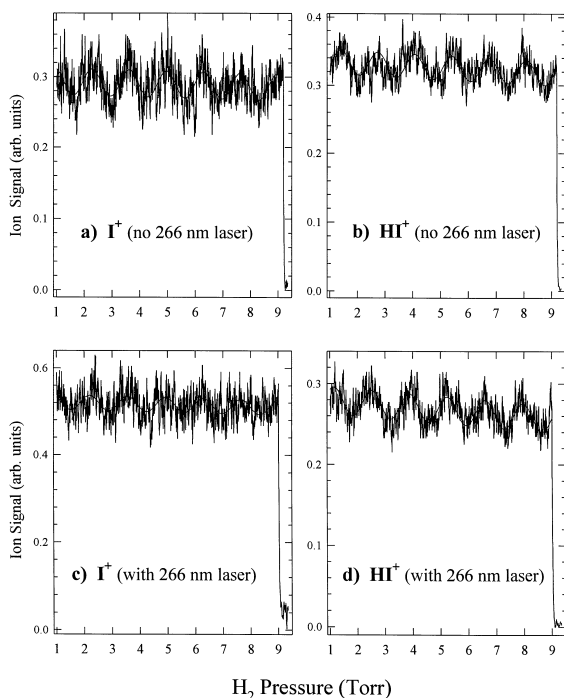


Fig. 4. Modulation of I^+ and HI^+ signals produced without (a,b) and with (c,d) the 266 nm pulse preceding the UV and VUV control pulses. The smooth curves are least squares fits of Eq. (2).

where θ is proportional to the H_2 pressure in the phase-tuning cell, A is the non-modulated (background) part of the signal, and B is the amplitude of the modulated part of the signal. The modulation depth is given by

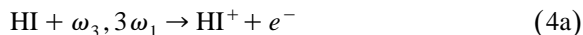
$$\frac{B}{A} = \frac{I_{MAX} - I_{MIN}}{I_{MAX} + I_{MIN}}, \quad (3)$$

where I_{MAX} and I_{MIN} are, respectively, the maximum and minimum intensity of the modulated signal. The average values of the fitted parameters obtained from four sets of scans are listed in Table 1. In this table, A and B refer to the scans recorded without the dissociation pulse, whereas A_{266} and B_{266} refer to runs with the dissociation pulse. These numbers indicate that the 266 nm laser pulse depletes the density of the HI molecules in the control volume by $\approx 20\%$. This effect is observed in both the modulated and non-modulated parts of the HI^+ signal and in the modulated part of the I^+ signal. We also observed that the phase lag between the HI^+

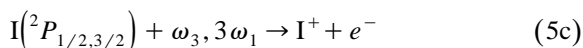
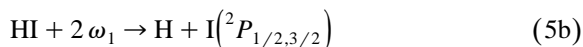
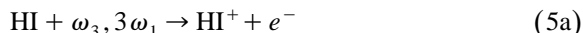
and I^+ signals was unaffected by the dissociation laser.

As described in Section 1, the two mechanisms considered are:

Mechanism 1:



Mechanism 2:



The results in Table 1 strongly support Mechanism 1 in two ways. First, if Mechanism 1 were correct, we would expect the decrease in the concentration of excited HI molecules caused by the prepulse to reduce the amplitude of the modulated I^+ signal (i.e. $B_{266}/B < 1$) and to increase the unmodulated background ($A_{266}/A > 1$), whereas if Mechanism 2 were correct, we would expect the increased concentration of $I(^2P_{1/2,3/2})$ to cause the modulated I^+ amplitude to increase ($B_{266}/B > 1$). The last two columns in Table 1 clearly show that the former is the case. Second, if the modulated I^+ signal was a result of controlling the ionization of ground state I atoms (Mechanism 2), one would expect the modulation depth of the I^+ signal to remain relatively unaltered in the presence of more ground state iodine. If Mechanism 1 prevails, however, one would expect the modulation depth of the I^+ signal to decrease because of the increased background from atomic iodine. Comparison of the columns 2 and 3 of the table clearly shows that the latter is true.

Table 1
Ratios of least squares fits of the modulation parameters defined in Eq. (2)^a

Ion	B/A	B_{266}/A_{266}	B_{266}/B	A_{266}/A
HI^+	0.054 ± 0.003	0.055 ± 0.03	0.79 ± 0.10	0.78 ± 0.05
I^+	0.066 ± 0.008	0.031 ± 0.003	0.78 ± 0.13	1.59 ± 0.14

^aThe ratios are averages of multiple scans, with uncertainties of a single standard deviation.

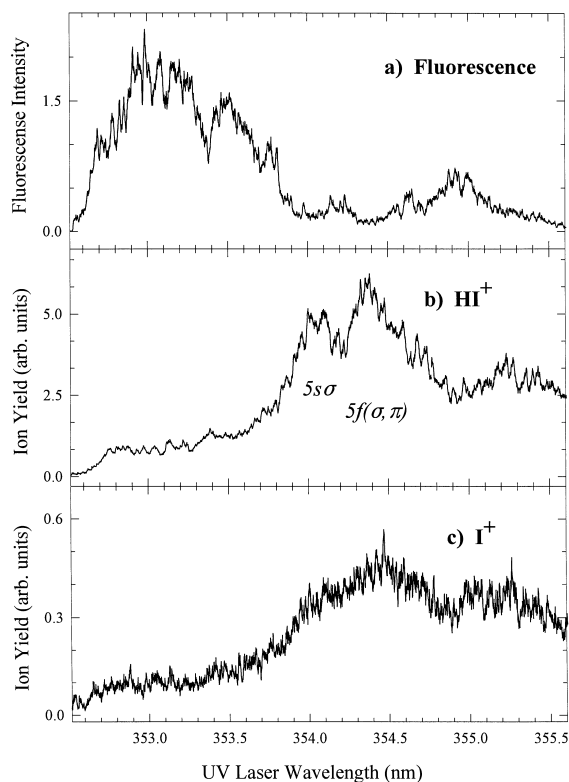


Fig. 5. Rapid scan of the fluorescence (a) and MPI (b,c) spectra of HI. The molecules were excited with a single photon of VUV radiation (at one-third the wavelength shown in the abscissa).

3.2. Fluorescence experiment

A rapid scan of the one-photon (VUV) fluorescence excitation is shown in Fig. 5a, and an expanded portion of the spectrum in the vicinity of the $5s\sigma$ resonance of HI is shown in Fig. 6a. In the bottom two panels of these figures are shown the HI^+ and I^+ one-photon ion spectra measured with the TOF machine.¹

Although the source of the fluorescence could conceivably be emission from excited HI or DI

¹The MPI spectra in Fig. 6 are the average of 10 scans, whereas the broadband data in Fig. 5 are the average of 4 scans. Discrepancies between the relative amplitudes of some of the peaks in these spectra are attributed to the lower accuracy of the latter. The anti-correlations between the fluorescence and ionization signals discussed in the text are nevertheless present in both figures.

molecules, we rule out this possibility by the following two-step argument. First, we note that the fine structure in all three spectra has a width of approx. 2 cm^{-1} . (This structure is of rotational origin.) From this width we deduce that the lifetime of the excited parent molecule is approx. 3 ps. This lifetime is indicative of a radiationless process (predissociation or autoionization), inasmuch as the radiative lifetime is $\geq 885 \text{ ps}$ for an oscillator strength $f \leq 1$ [11]. It follows that the molecular fluorescence rate is at least three orders of magnitude slower than the radiationless rate. Second, we note in Fig. 6 that many of the peaks in the fluorescence scan correspond to minima in the molecular ion spectrum, and vice versa. A simple kinetic model shows that if the fluorescence rate is much slower than ionization, the fluorescence signal should track the ionization signal, whereas if the two rates are comparable the signals should be anti-correlated. Close examination of the structure in Fig. 5a,b reveals that many of the maxima in one spectrum correspond to minima in

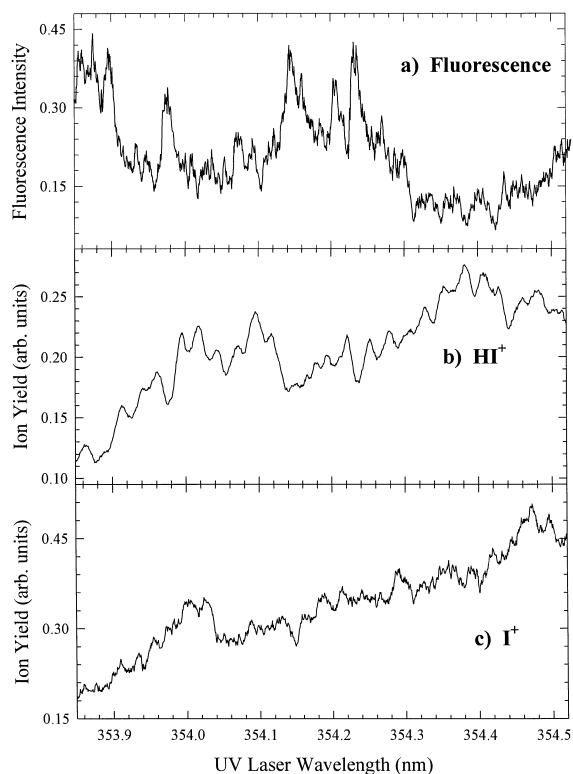


Fig. 6. Expanded scan of the fluorescence and MPI spectra of HI.

the other, and vice versa. Since in fact the fluorescence rate is much slower than ionization and/or dissociation, the anti-correlation observed in the spectra implies that the fluorescence signal cannot be of molecular origin.

If the fluorescence is not molecular in origin, it must result from emission by atomic iodine. (The $\omega_3/3\omega_1$ photon energy is insufficient to produce $H(n=2) + I$ products, and no H^+ signal was observed.) The fluorescence data therefore provide direct evidence of a predissociation channel, as was postulated for Mechanism 1. The anti-correlation between the fluorescence and HI^+ signals is readily explained if the competing processes of autoionization and predissociation have comparable rates. The weak correlation between the fluorescence and the I^+ signals may be explained if some of the I^+ signal is produced by secondary photodissociation of HI^+ , by the UV (355 nm) laser in addition to photoionization of I^* . The former is correlated to the production of HI^+ , whereas the latter may be anti-correlated with HI^+ .

In conclusion, we have presented two direct pieces of evidence that the phase lag we observed between the HI^+ and I^+ signals produced by one- and three-photon excitation of HI is the result of coherent control of the branching of competing decay processes (autoionization versus predissociation) in the same molecule. The first experiment, photodissociation of the parent molecule by a prepulse did not increase the modulation amplitude of the I^+ signal, thereby ruling out the possibility that modulation of the I^+ signal comes from coherent control of atomic fragments (Mechanism 2). The second experiment provides direct evidence for the existence of a predissociation path at the excitation energy ($3\omega_1$) of the control experiment. This is an important point

because the detailed shape of the potential energy curve for the predissociating $^3\Pi_0$ Rydberg state is unknown. We note in closing that if Mechanism 2 were correct, we would infer that the phase lag results from the difference between δ_{13}^S for the ionization of HI and the ionization of I. This conclusion would contradict the theoretical finding [12,13] that the molecular phases cancel out in both ionization processes.

Acknowledgements

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