Quantum yields of fragments in 193 nm photodissociation of KI

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Following 193 nm photodissociation of KI, a three-photon (2+1) resonance-enhanced multiphoton ionization (REMPI) technique is employed to probe the nascent I fragment as partitioned in its two lowest fine-structure states. It is found that the quantum yield of the ground state $I(5\,^2P_{3/2})$ amounts to 97 ± 3%. This result and previous observations indicate that the accompanying partner K atom is predominantly partitioned to the $5\,^2P_J$ state, while the fragment in the lower states can be negligible.

1. Introduction

Photodissociation of diatomics has been widely used to generate hot fragments, with which investigation on the kinetic energy dependence of a chemical reaction can be carried out. To control sufficiently the energy carried in a reaction, it is crucial to understand thoroughly the quantum yields of the fragments concerned. In the radiative lifetime measurement of an alkali atom, luminescence detection of the excited alkali fragment following photodissociation of its halides provides advantage of avoiding the effect of radiation trapping [1,2]. In addition, a practical application of such a method can lead to population inversion of the photofragments, upon which the production of atomic resonance lasers becomes accessible. For instance, Ehrlich and Osgood [3] have demonstrated that alkali atomic resonance lasers have been successfully generated through the photodissociation of various alkali halides. The energy-conversion efficiency they have obtained lies in the range 1–3%; thus the output power amounts to 1–10 kW.

Upon irradiation of the KI vapor with a 193 nm laser, more than 80% K fragment partitioned into the $5\,^2P_J$ state has been reported [4]. In a relative fluorescence measurement of the photofragment $K(5\,^2P_J)$ as a function of excitation wavelength, Earl and Herm [2] have revealed that the profile was peaking around 193 nm. Using a time-of-flight technique, it has been found that the KI photodissociation with 265–295 nm gives rise mostly to the excited state fragment $I(5\,^2P_{1/2})$; while for the excitation wavelength above 305 nm, the ground state $I(5\,^2P_{3/2})$ becomes predominant [5]. The photon energy from 193 nm laser can overcome the dissociation energy of KI and also provide extra energy for excitation of the fragment K to the $5\,^2P_J$ state [6]. In the center-of-mass frame, the translational energy ϵ available to the fragments can be estimated by [6]

$$\epsilon = h\nu(193\ \text{nm}) - D_0 - E^* , \qquad (1)$$

where D_0 is the dissociation energy of KI and E^* is the internal energy of the fragments. Accordingly, the excess energy for the exit channel, $K(5\,^2P_J) + I(5\,^2P_{3/2})$, is about 500 cm^{-1}, provided that the KI is in its ground vibrational state.

For determining the quantum yields of the photofragments in different electronic states, the relative intensity measurement of emission signal as a result of individual excited fragment is not very efficient. For instance, in the 193 nm photodissociation of KI, the K atoms are expected to be fragmented into various states. For the excited states with long lifetimes, the fluorescence signal may be obscured by the effect of population redistribution. Analogously, in the quantum yield measurement of the excited $I(5\,^2P_{1/2})$ atom by means of fluorescence detection,

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the collisional deactivation process can interfere the observation of IR emission having a radiative lifetime as long as 0.13 s.

In an attempt to acquire a more accurate value for the yields of photofragments than that obtained by the fluorescence method, we have employed a resonance-enhanced multiphoton ionization (REMPI) technique in this work to monitor the fragmented I atoms following 193 nm photodissociation of KI. The iodine ions in the $I(5\,^2P_{3/2})$ (or $I(5\,^2P_{1/2})$) state have been detected by the (2+1) REMPI scheme through the $^2D_{5/2}$ (or $^2D_{3/2}$) intermediate states. Based on this method, the populations of the nascent I fragment in its fine-structure components can be determined; furthermore, information about the nascent K atoms' state distribution may also be inferred.

2. Experimental

Since the experimental setup, especially for the fluorescence measurement in a heat-pipe oven, has already been illustrated elsewhere [7–9], only the part of REMPI apparatus will be described below and schematized in fig. 1.

The radiation sources for the REMPI apparatus contained one ArF excimer laser for photolysis of the KI sample, and the other excimer laser-pumped dye laser, tunable in the range 588–644 nm with rhodamine B dye, to monitor the fragmented I atoms. The pulse durations for both lasers are of 15–20 ns. The delay time between them was kept to be less than 80 ns. Since the system pressure was kept below 10 mTorr during the REMPI experiment, the iodine ions probed in the short delay time can be considered to be under collision-free condition. The dye laser was tuned either across the iodine atomic two-photon transition $5\,^2P_{3/2}\rightarrow{}^2D_{5/2}$ at 304.7 nm or across $5\,^2P_{1/2}\rightarrow{}^2D_{3/2}$ at 306.7 nm; one additional photon can subsequently photoionize the excited I atoms. The three-photon (2+1) REMPI scheme is depicted in fig. 2. The output energy of 193 nm laser was kept about 1 mJ, so that the multiphoton absorption effect may be eliminated; and the dye laser was 2–3 mJ throughout the experiment.

The pure KI sample was deposited in a five-armed heat-pipe oven, operated at 673±2 K; thus the vapor pressure corresponded to 0.8 mTorr [10]. The reactor was evacuated below 10^{-5} Torr and purged with the inert gas Ar several times, so that the collisional deactivation process may be negligible. A pair of stainless-steel electrodes, positioned 1 cm apart, was inserted through the top arm of the oven for col-

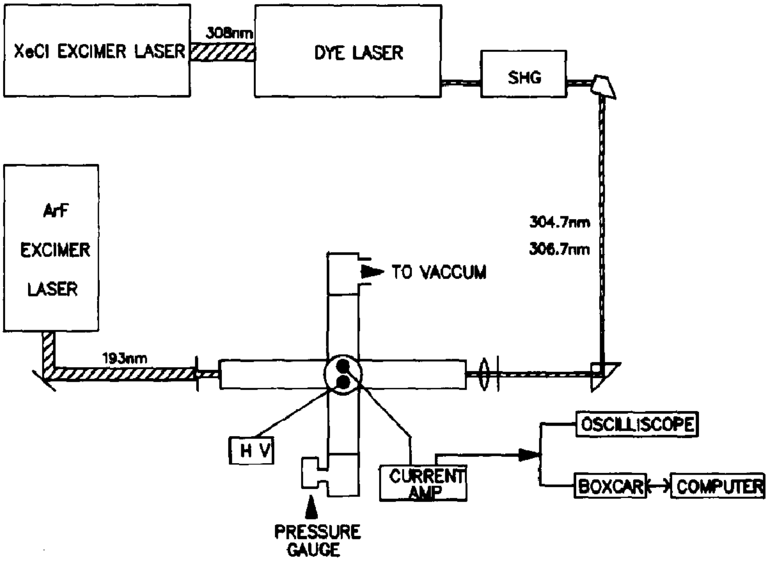

Fig. 1. Schematics of the REMPI apparatus.

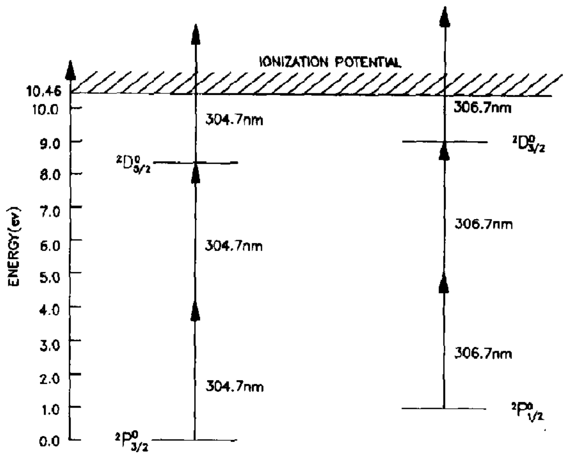

Fig. 2. The three-photon (2+1) REMPI energy scheme for probing the I fragments in their ground and spin–orbit excited states.

lection of the iodine ions produced. The collected signal was amplified with a current amplifier, and then fed into a boxcar integrator for the improvement of the signal-to-noise ratio before the result was output to a strip-chart recorded or stored in a microcomputer.

3. Results and discussion

As shown in fig. 3, the signals for iodine ions, populationed in the ground and their spin–orbit excited states, are obtained using the (2+1) REMPI technique through $^2D_{5/2}$ and $^2D_{3/2}$ as intermediate states respectively. Because the iodine fine-structure components are the only exit channels following photodissociation, the quantum yield of $I(5\,^2P_{3/2})$ is defined as $S(P_{3/2})/[S(P_{3/2})+S(P_{1/2})]$. Here $S(P_{3/2})$ and $S(P_{1/2})$ are the populations of the nascent I fragment in its two fine-structure states. The following equation can be used to relate the ion signals to the relevant state populations:

$$\frac{\mathrm{ion}(P_{1/2})}{\mathrm{ion}(P_{3/2})}=k\frac{S(P_{1/2})}{S(P_{3/2})}\,. \tag{2}$$

Using the excitation scheme identical with our work, Bersohn and co-workers [11] have detected the laser-induced VUV fluorescence from the excited I atoms in the experiment of CH_3I photodissociation, and subsequently derived a calibration factor, $k=1.12$, for such an iodine probing scheme. We adopt the same calibration factor in eq. (2), assuming that the I atoms excited to both $^2D_{5/2}$ and $^2D_{3/2}$ states have the same ionization cross section. Then we obtain the quantum yield of $I(5\,^2P_{3/2})$ resulting from the

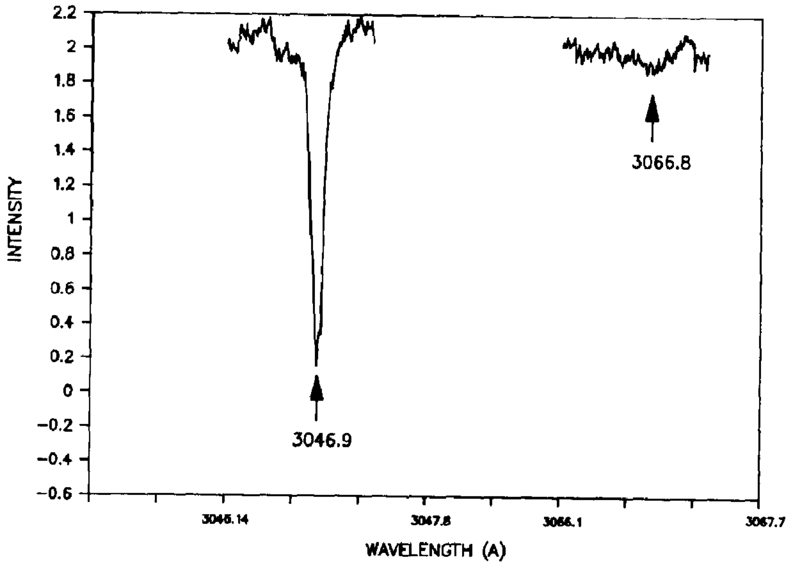

Fig. 3. The REMPI signals for $I(5\,^2P_{3/2})$ and $I(5\,^2P_{1/2})$ atoms obtained following the scheme described in fig. 2.

KI 193 nm photodissociation as 97 ± 3% for the first time. In the case of alkyl iodide photodissociation, it has been found that the electron-withdrawing groups may lead to a dominant I fragment in the spin–orbit excited state, whereas the electron-donating groups favor the I fragment in its ground state [11–13]. It is interesting to note that in the current work the K atom as an electron-donating partner happens to follow the same trend.

While scanning a monochromator over the region 300–900 nm following the KI photodissociation, we have observed only two emission lines for the transition $5\,^2P_J \to 4\,^2S_{1/2}$ at 404 nm and $4\,^2P_J \to 4\,^2S_{1/2}$ at 769 nm. As corrected with the spontaneous emission coefficients and the instrumentation sensitivity, the peak at 404 nm relevant to the $5\,^2P_J$ population dominates much over the other peak relevant to the $4\,^2P_J$ population. Since the lifetime 137 ns for the $5\,^2P_J$ state is much longer than about 26 ns for $4\,^2P_J$ [1,2], the observed small signal may be attributed to the population redistribution from the upper states. It is evidenced by the fact, reported by Schilowitz and Wiesenfeld [4], that the rise time of time-resolved fluorescence for the transition from $4\,^2P_J$ to $4\,^2S_{1/2}$ is much slower than that for the transition from $5\,^2P_J$ to $4\,^2S_{1/2}$.

Provided that $K(4\,^2P_J)$ and $K(4\,^2S_{1/2})$ are also fragmented, the iodine atom populated to its spin–orbit excited state becomes energetically accessible. The K atoms in the $4\,^2P_J$ state, for instance, would have excess energy ≈ 12000 cm^{-1}, enough to compensate for the energy defect between the $I(5\,^2P_J)$ doublets, about 7603 cm^{-1} [14]. It seems unlikely that the excess energy carried by these lower states would be totally transferred into the translational energy, but not partly into the internal energy of the iodine atoms. In probing the femtosecond dynamics, of NaI photodissociation the very early stage of cleavage process shows that the NaI diatom is bounced back and forth in a quasi-potential well, adiabatically formed from an excited repulsive covalent potential curve and an ionic potential curve [15]. The result leads to a leaking about 10% yield of the Na atom each period. Obviously, the NaI diatom in the photodissociation process is exposed simultaneously upon both repulsive and attractive forces, and consequently retarded to break apart. Having a similar character with NaI, the behavior of KI photodissociation seems hardly to be fitted in the impulsive model [16–18]. Based on this model, the KI sample is expected to break apart abruptly upon laser irradiation, as if a repulsive force exerts upon it; thereby the excess energy carried by the fragments is otherwise converted completely into translational energy [16–18]. Accordingly, the observed extremely large quantum yield for the $I(5\,^2P_{3/2})$ state implies that the dissociation channels into the lower states, especially for the $4\,^2P_J$ and $4\,^2S_{1/2}$, can be negligible. Besides, Schilowitz and Wiesenfeld have previously measured the time-resolved fluorescence for individual excited K fragment in the 193 nm photodissociation of KI, and found that more than 80% K fragment is scattered to the $5\,^2P_J$ state, but insignificant amount contributed to the 3D and 5S states within their detection conditions [4]. This has also been verified in a later experiment on the pressure dependence of the $4\,^2P_J \to 4\,^2S_{1/2}$ fluorescence detection [19]; based on an assumption that the initial fragments in the 3D and 5S states are zero, the theoretical prediction is in excellent agreement with the above experimental results. Therefore, we may conclude from the above observations that the accompanying potassium atoms are predominantly partitioned to the $5\,^2P_J$ state. It is also noted that the higher-state K fragments than $5\,^2P_J$ could not be detected within our detection limit.

In summary, using a three-photon REMPI technique, we have measured a quantum yield of 97 ± 3% for I atoms partitioned in their ground state following the KI photodissociation with a 193 nm excimer laser. This result and previous observations [4,19] indicate that the accompanying K atoms are predominantly partitioned to the $5\,^2P_J$ state, while K fragment in the lower states can be negligible.

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