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Multiphoton Ionization of Molecules*†

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This work reports the first attempt at multiphoton ionization of molecules of iodine, heavy water, and carbon tetrachloride. Despite the occurrence of many different ions, only I^+, D^+, and CCl_3^+, respectively, were observed quantitatively using the technique of multiphoton ionization of atoms. "Saturation" was observed.

I. INTRODUCTION

Multiphoton ionization of atoms has been reported by many workers, both theoretically and experimentally.[1-6] But so far, to the best of our knowledge no work has been done on the multiphoton ionization of molecules, although there has been some work on multiphoton dissociation.[7,8] This work presents a first attempt experimentally to investigate multiphoton ionization of molecules.

It is generally agreed that the probability per unit time P of ionizing an atom by "simultaneously" absorbing k optical photons in an intense laser radiation (flux F cm^{-2} sec^{-1}) is proportional to F^k,

$$P = W_k F^k , \tag{1.1}$$

where W_k is the kth-order cross section. Usually, however, experimental verifications involve the ionization of atomic gases.[2,4-6] This creates a side effect, namely, substantial depletion of the neutral atoms.[3] The result[2] is that the experimental plot of $\log_{10} P$ vs $\log_{10} F$ will have a slope less than k. This depletion ("saturation") was also observed in the present work for molecules.

II. EXPERIMENT

The experimental method was the same as that employed in multiphoton ionization of atomic gases.[2,9] A 100-MW ruby laser was focused into a vacuum system into which different molecular gases were leaked. The ions created were analyzed by a time-of-flight mass spectrometer.

The following molecular vapors were used: I_2, D_2O, and CCl_4. The quantitative measurements were carried out in the same way as those customarily employed in atomic gases; i.e., the number of ions created was plotted against the laser flux in log-log plot.[2,4-6,9]

III. RESULTS AND DISCUSSIONS

A. I_2 Vapor

Only I^+ ions were observed when the ruby laser was focused into an I_2 vapor of $\sim 10^{-5}$ torr. Figure 1 shows the log-log plot of N/τ vs F_0, where N is the number of ions created in the focal region, τ, the width of the laser pulse of half-maximum, and F_0 the peak laser flux. The saturation is evident in the plot.

The fact that only I^+ ions were observed would mean that I_2 could have been broken up through one or more of the following ways[10]:

$$I_2 + k_1 h\nu \rightarrow I_2^+ + e \tag{3.1}$$

followed by

$$I_2^+ + k_2 h\nu \rightarrow I^+ + I ,$$

or

$$I_2 + k_3 h\nu \rightarrow I + I \tag{3.2}$$

followed by

$$I + k_4 h\nu \rightarrow I^+ + e ,$$

or

$$I_2 + k_5 h\nu \rightarrow I^+ + I^- . \tag{3.3}$$

All the k's are integers and $h\nu$ is the ruby photon energy. The partial slope (~ 6) of Fig. 1 suggests that the formation of I^+ from any of the above three processes requires the absoprtion of six ruby-laser photons.

The ionization potential of an iodine atom is 10.6 eV, which lies between five and six ruby-laser photons. It thus suggests to us that I^+ would prob-

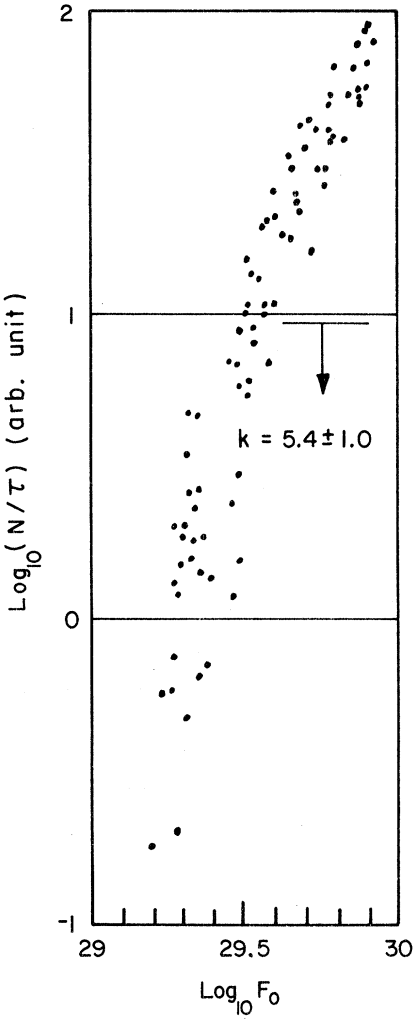

FIG. 1. Log-log plot of I^+ from I_2.

ably come from the sixth-order multiphoton ionization of I. This means that the second process would be the probable one; i.e., the molecule would dissociate into atoms during the initial part of the laser pulse, and then the atoms of iodine would be multiphoton ionized. Since the dissociation energy of I_2 is only 1.542 eV[11] (less than one ruby-laser photon energy, 1.785 eV), it is highly probable that all I_2 in the focal region were dissociated via one-photon absorption during the initial part of the laser pulse. That is to say, this nearly complete dissociation would give a near-unity dissociation probability. Hence, the total probability of obtaining an I^+ ion via the second process would become

$$P = P_D P_i \simeq P_i = W_6 F^6 ,$$

where P is the total probability, P_D the dissociation probability which is approximately unity, and P_i the probability of six-photon ionization of I. In what follows, whenever a process consists of several successive multiphoton processes, the probability of those l-photon processes ($l \leq 3$) will be assumed to be unity. This assumption is based on the following estimation. From Bebb's work[12] the theoretical cross section for three-photon ionization of a potassium atom by a ruby laser is $W_3 \sim 10^{-79}$ cm^6 sec^2. The normal laser flux used in the present work was $F_0 \sim 10^{29.5}$ cm^{-2} sec^{-1}, and the half-width of the laser pulse was $\tau \sim 10^{-8}$ sec. Using Eq. (1.1), the total probability of three-photon ionization would then be $W_3 F_0^3 \tau \sim 10^{1.5} > 1$. For two- or one-photon processes under the same conditions, the total probability would be larger. (See also Ref. 13.)

On the other hand, the minimum energy needed for the third process is (neglecting the kinetic energy)

$$E = d(I_2) + i(I^+) - a(I^-) , \qquad (3.4)$$

where d is the dissociation energy, $i(I^+)$ the first ionization potential of I, and a the electron affinity of I forming I^-. These energies add up to give $E = 9.054$ eV.[14] This is also between the energy of five and six ruby-laser photons. The partial slope of Fig. 1 indicates that the third process would also be a probable one.

It is not possible to check whether this process exists by observing I^- ions, since the electron affinity of I (3.07 eV) is so small that any I^- formed would immediately have the electron detached by the intense radiation via two-photon absorption.[13] This applies to the case of other molecules.[15]

Moreover, the ionization potential of I_2 forming I_2^+ is 9.35 ± 0.03 eV[16] which lies between the energy of five and six ruby photons. Since the dissociation energy of I_2^+ into I^+ and I is $\simeq 4.8$ eV, which is less than three ruby photons, the high-intensity radiation would very quickly dissociate all I_2^+ so formed. This not only explains why no I_2^+ ions were observed, but also indicates that the first process could also be responsible for producing I^+ ions, but probably to a lesser degree.

As a result, the computation of the cross section is not necessary because there are so many competing indistinguishable processes taking place simultaneously. This situation applies to other molecules in later sections.

B. D_2O Vapor

When the laser was focused into D_2O vapor, many ions were formed. They were D^+, O^+, OH^+, H_2O^+, OD^+, and D_2O^+. OD^+ and H_2O^+ were almost on top of each other. The intensity of D_2O^+ was the highest. The intensities of D^+ and $(OD^+ + H_2O^+)$ were similar, each about two-thirds that of D_2O^+, while those of O^+ and OH^+ were the lowest, about half that of D_2O^+.

OH^+ and H_2O^+ might come from the heavy water

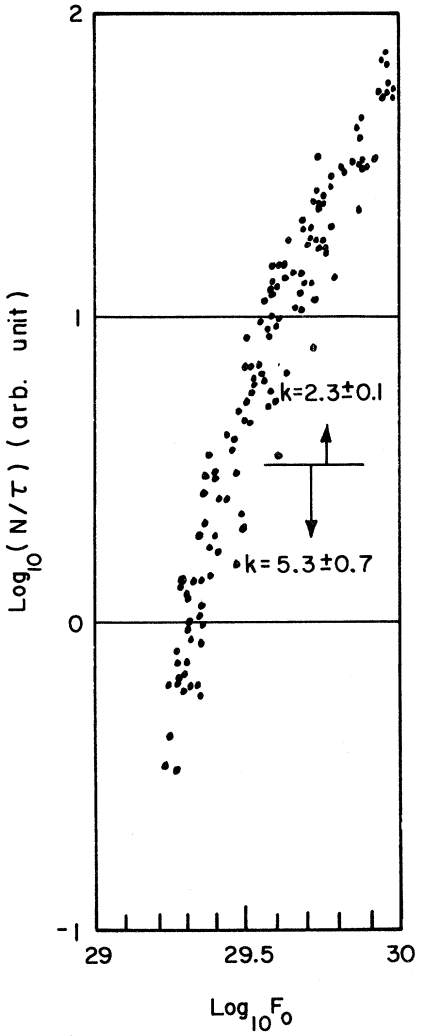

FIG. 2. Log-log plot of D^+ from D_2O.

(minimum isotope purity, 99.7-at.% D) and from the replacement of D by H in the vacuum system before ionization. We neglect these impurities. We then have, in descending order of intensity, D_2O^+, D^+, OD^+, and O^+.

Unfortunately, these signals were only resolvable using a rather long time-of-flight path (35 cm) in which there was considerable ion loss. As a result the signals were too small to yield good quantitative observations. (One can see that the vapor pressure could not be raised too high because recombination would then be important.) Using a shorter time-of-flight path (10 cm) so as to collect most of the ions, O^+, OD^+, and D_2O^+ were all mixed together in the background hydrocarbon noise[9] and could not be resolved properly. Hence, only D^+ was observed quantitatively.

Figure 2 shows the experimental results of D^+ from focusing the laser into D_2O vapor at a pressure of about 2.9×10^{-5} torr. The log-log plot is very different from those of other ions. It shows saturation effects almost at the beginning of the flux range. The slope of the bottom part of the plot is 5.3 ± 0.7, while that of the upper part is 2.3 ± 0.1.

To see that the log-log plot in Fig. 2 shows early "saturation," let us look into the possible reactions leading to D^+. They are shown in Table I.[17] There are five major processes, each of which will eventually lead to D^+ ions. If we assume that each process resembles the multiphoton ionization of an atom, the minimum number of photons required is at least 7, via process (2); i.e., the slope of the log-log plot should be at least 7. However, it shows a much lower value. Note that the change of slope appears to begin at $F_0\sim10^{29.4}$ cm^{-2} sec^{-1} (Fig. 2), while that for seven-photon ionization of Xe begins at $F_0\sim10^{29.7}$ cm^{-2} sec^{-1}.[2] The relatively low laser flux at which a change of slope occurs should not cause any appreciable "saturation." The fact that it did indicates a high-ionization cross section, and hence, a large ionization probability. This could be caused by some complicated resonance

TABLE I. Possible reactions leading to D^+ in the interaction of D_2O with high-intensity ruby-laser radiation.

	Reactions	Minimum energy required
(1)	$D_2O\rightarrow D+OD$	5.16 eV = 2.89$h\nu$[a]
	followed by	
(a)	$D\rightarrow D^+ + e$	(13.6 eV) = 7.62$h\nu$
(b) (i)	$OD\rightarrow O+D$	4.81 eV = 2.69$h\nu$
(ii)	$OD\rightarrow O^- + D^+$	16.91 eV = 9.47$h\nu$
(iii)	$OD\rightarrow OD^+ + e$	(13.8 eV) = 7.73$h\nu$
	$OD^+\rightarrow O+D^+$	4.81 eV = 2.69$h\nu$
(2)	$D_2O\rightarrow D_2O^+ + e$	12.6 eV) = 7.05$h\nu$
	followed by	
	$D_2O^+\rightarrow D^+ = OD$	5.16 eV = 2.89$h\nu$
	followed by process (1b)	
(3)	$D_2O\rightarrow D^+ + OD^-$	16.93 eV = 9.5$h\nu$
	followed by	
	$OD^-\rightarrow OD + e$	1.835 eV = 1.03$h\nu$
	followed by process (1b)	
(4)	$D_2O\rightarrow D_2 + O$	
	followed by	(5.0 eV) = 2.8$h\nu$
(a)	$D_2\rightarrow D+D$	
	followed by (1a)	(4.476 eV) = 2.5$h\nu$
(b)	$D_2\rightarrow D_2^+ + e$	(15.6 eV) = 8.74$h\nu$
	followed by	
	$D_2^+\rightarrow D+D^+$	(4.476 eV) = 2.5$h\nu$
(5)	$D_2O\rightarrow D_2^+ + O^-$	(19.1 eV) = 10.7$h\nu$
	followed by	
	$D_2^+\rightarrow D^+ + D$	(4.476 eV) = 2.5$h\nu$

[a] $h\nu$ = 1.785 eV = energy of one ruby-laser photon.

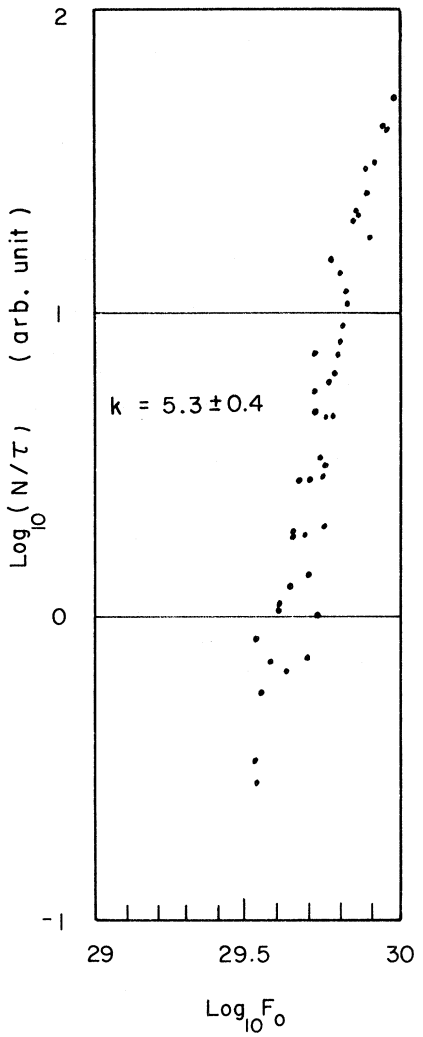

FIG. 3. Log-log plot of CCl_3^+ from CCl_4.

processes in the complex molecule. The result is an early depletion of neutral molecules.

C. CCl_4 Vapor

The ions created in CCl_4 vapor at $\sim 10^{-4}$ torr were observed. In order of decreasing abundance, they were CCl^+, CCl_3^+, Cl^+, and CCl_2^+. No CCl_4^+ was observed. As in the case of D_2O, only CCl_3^+ could be properly observed quantitatively. The rest were mixed with the background ions.[9] Figure 3 shows the log-log plot of CCl_3^+. No saturation can be seen from the plot. The slope is 5.3 ± 0.4. This means that a five-photon process has been involved. However, the laser flux at which appreciable number of ions were collected is higher than that of the six- and seven-photon ionization of Hg and Xe, respectively.[2]

There are two more probable reactions leading to CCl_3^+. They are

$$CCl_4 \rightarrow CCl_3 + Cl, \quad CCl_3 \rightarrow CCl_3^+ + e\,, \tag{3.5}$$

$$CCl_4 \rightarrow CCl_3^+ + Cl^-\,. \tag{3.6}$$

Let us consider them separately.

In the first process, although the dissociation energy CCl_3-Cl is only 3.0 ± 0.1 eV,[17] which is between one and two times the ruby-laser photon energy, the cross section may be very small, as commented upon in Ref. 7, owing to the homopolarity of CCl_4. Hence, higher flux may be required to dissociate it substantially. The CCl_3 radicals created would then be five-photon ionized (the ionization potential of CCl_3 is 8.78 eV[17]). Hence, the log-log plot (Fig. 3) starts at a higher laser flux than the six- or seven-photon process,[2] even though it is only a five-photon process.

In the second process the minimum energy required [see Eq. (3.4)] is 8.17 eV,[14] which is also between the energy of four and five ruby-laser photons. Hence, this process would also be responsible for the five-photon ionization process.

It is interesting to point out that no CCl_4^+ was observed even though this involved only a seven-photon process (the ionization potential of CCl_4 is 11.47 eV).[18]

IV. CONCLUSION

Multiphoton ionization of molecules using a high-power ruby laser is complicated by many competing processes, namely, dissociation, dissociative ionization, and ionization of the molecules and dissociated fragments, etc. The usual experimental method employed in the multiphoton ionization of atoms cannot resolve these processes properly.

ACKNOWLEDGMENT

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Delayed-Coincidence Study of O^+-Xe Collisions at 50–210 keV*

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Delayed-coincidence techniques have provided measurements of $\bar{Q}(r_0)$ for O^+-Xe collisions in the energy range 50–210 keV; here r_0 represents the distance of closest approach of the colliding particles, and $\bar{Q}$ is the average energy transferred to inelastic processes. At fixed r_0 the $\bar{Q}$ values increase with bombarding energy. The $\bar{Q}$ values generally increase as r_0 decreases although they remain constant over some regions of r_0 within the range (0.05–0.25 Å) covered by the experiment. The r_0 regions in which $\bar{Q}$ increases appear to be correlated with regions in which the differential cross sections for beam-particle scattering fail to vary according to the predictions of the exponentially screened Coulomb potential. Simple interpretations of the data attribute these results to the effects of electronic shell interpenetrations during the collisions. Supplementing the $\bar{Q}$ and cross-section data are determinations of average ionic charge states after collision and calculations of inelastic energy-loss cross sections deduced from the $\bar{Q}$ results.

I. INTRODUCTION

Among recent experimental studies of close-encounter collisions between heavy atomic species are several investigations of collisions induced by O^+ projectiles.[1–3] This paper is the third in a series dealing with collisions between O^+ ions and rare gases. The two previous studies showed some striking differences between the inelastic collision properties of the O^+-Ar and O^+-Ne systems.[1,2] Extension of this series to O^+-Xe collisions should reveal further insights into the systematics of collisions between O^+ ions and noble gases. Additional data on such collisions are available in the work of Knystautas, Kessel, Del Boca, and Hayden,[3] who have studied the O^+-Kr system.

This experiment, like its predecessors, has the primary purpose of elucidating details of inelastic processes (excitation, ionization, photon production). For this purpose the experimental results include four kinds of data: kinetic energy transferred to inelastic channels, differential cross