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Competition Between Two Excitation-dissociation Channels for Molecular Ions

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When the molecular ions XYZ^+ ($XY_2{}^+$) are excited simultaneously from an electronic state E_0 into two higher electronic states E_α and E_β with supervened dissociation or predissociation, competition between the α and β excitation-dissociation channels occurs. A theoretical model is provided to deal with the competition of the two excitation-dissociation channels with more than two kinds of ionic products for XYZ^+ ($XY_2{}^+$). Supposing that the photo-excitation rates of two states E_α and E_β are much less than their dissociation or pre-dissociation rates, a theoretical equation can be deduced to fit the measured data, which reflects the dependence of the product branching ratios on the intensity ratios of two excitation lasers. From the fitted parameters the excitation cross section ratios are obtained. In experiment, we studied the competition between two excitation-dissociation channels of $CO_2{}^+$. By measuring the dependence of the product branching ratio on the intensity ratio of two dissociation lasers and fitting the experiment data with the theoretical equation, excitation cross section ratios were deduced.

Key words: Molecular ion, Competition of two excitation channel, Photodissociation, Excitation cross section ratio

I. INTRODUCTION

The study of photodissociation dynamics of molecules (including molecular ions) can provide useful information on the interaction between the electronic states of molecules, and the breaking of bonds to form fragment products, etc. [1,2]. The branching ratio of the ionic fragments related to the excited potential surface of molecules is one of the most important parameters in the study of the photodissociation dynamics of small molecular ions, such as $CS_2{}^+$ and $CO_2{}^+$ [3,4]. For example, Hwang *et al.* measured the product branching ratio ($[S^+]/[CS^+]$) in the study of the predissociation of $CS_2{}^+(\widetilde{C}^2\Sigma_g^+)$ and found that the $[S^+]/[CS^+]$ value for bend vibration levels is slightly larger than that for the levels with symmetry stretching vibration [5]. In our previous study, we obtained the photofragment excitation (PHOFEX) spectrum of $CS_2{}^+$ by using one color [1+1] two photon dissociation via $\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+(000,100)\leftarrow\widetilde{X}^2\Pi_{g,3/2}(000)$ transitions [6], and by using two color [1+1′] two photon dissociation via $\widetilde{C}^2\Sigma_g^+(000,100)\leftarrow\widetilde{B}^2\Sigma_u^+(000,100)\leftarrow\widetilde{X}^2\Pi_{g,3/2}(000)$ transitions [7]. It was found that the product branching ratio $R=[S^+]/[CS^+]$ for the [1+1] process obviously differs from that of the [1+1′] process. When the first dissociation laser is introduced to excite the $\widetilde{B}^2\Sigma_u^+(000,100)\leftarrow\widetilde{X}^2\Pi_{g,3/2}(000)$ transitions and the second dissociation laser is introduced to excite the $\widetilde{C}^2\Sigma_g^+(000,100)\leftarrow\widetilde{B}^2\Sigma_u^+(000,100)$ transitions, the competition between the [1+1] and [1+1′] dissociation channels for $CS_2{}^+$ will occur. Hence, we studied the competition between the dissociation channel via $\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+$ transitions and the dissociation channel via the $\widetilde{C}^2\Sigma_g^+(000,100)\leftarrow\widetilde{B}^2\Sigma_u^+$ transitions for $CS_2{}^+$ [7]. With the measured dependence of the product branching ratios $R=[S^+]/[CS^+]$ on the intensity ratios $R_I=I_2/I_1$ of two dissociation lasers, the excitation cross section ratios of $R_\sigma=\sigma_C/\sigma_H$ have been fitted by using the theoretical equation provided in Ref.[1].

Departing from the simple situation of the two ionic products of S^+ and CS^+ in the dissociation of $CS_2{}^+$, in this work we propose a theoretical model to study the competition of the two excitation-dissociation channels with more than two kinds of ionic products, such as A^+, B^+, and C^+ for XYZ^+ ($XY_2{}^+$). Supposing that the photo-excitation rates of two states E_α and E_β are much less than their dissociation or pre-dissociation rates, the product branching ratios $R^{BA}=[B^+]/[A^+]$ and $R^{CA}=[C^+]/[A^+]$ measured in experiment will be dominated by the intensity ratios of two excitation lasers for the given molecular ions. By using the deduced theoretical formula to fit the measured R^{BA}-R_I and R^{CA}-R_I data, the excitation cross section ratios of can be obtained.

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II. THEORETICAL MODEL FOR THE COMPETITION OF TWO EXCITATION CHANNELS

Figure 1 shows a schematic diagram for the two excitation-dissociation channels of α and β for XYZ^+ (XY_2^+), which are related to the dissociation products of A^++a, B^++b, and C^++c. A^+, B^+, C^+ and a, b, c represent the ionic products and the related neutral products, respectively. Supposing that XYZ^+ (XY_2^+) are excited from the same lower electronic state of E_0 to the upper states of E_α and E_β by the absorptions of photon $h\nu_\alpha$ and $h\nu_\beta$, respectively, the relative excitation rates of W_α and W_β can be expressed as

$$W_\alpha = N_0\sigma_\alpha I_\alpha, \qquad W_\beta = N_0\sigma_\beta I_\beta \tag{1}$$

where N_0, σ, and I denote the population of lower state, the excitation cross section, and the laser intensity, respectively. Hence we have the ratio of excitation rates

$$R_W = \frac{W_\alpha}{W_\beta} = \frac{\sigma_\alpha I_\alpha}{\sigma_\beta I_\beta} = R_\sigma R_I \tag{2}$$

where $R_\sigma=\sigma_\alpha/\sigma_\beta$ and $R_I=I_\alpha/I_\beta$ denote the excitation cross section ratio and the intensity ratio of two related lasers for α and β excitation channels, respectively. Suppose that the upper state E_α of α channel is related to three dissociation paths with fragment products $A_\alpha{}^+$+a_α, $B_\alpha{}^+$+b_α, and $C_\alpha{}^+$+c_α, where $A_\alpha{}^+$, $B_\alpha{}^+$, and $C_\alpha{}^+$ denote the ionic products, a_α, b_α, and c_α denote the neutral products, respectively. There are also three dissociation products of $A_\beta{}^+$+a_β, $B_\beta{}^+$+b_β, and $C_\beta{}^+$+c_β related to the upper state E_β of β excitation channel, with ionic products of $A_\beta{}^+$, $B_\beta{}^+$, and $C_\beta{}^+$ and neutral products of a_β, b_β, and c_β, respectively. It is worth noticing that the real energy position of the states and the dissociation limitations for the molecular ions under study could be different from that shown schematically in Fig.1.

If the two channels of α and β are excited simultaneously and the resulting dissociation rates are

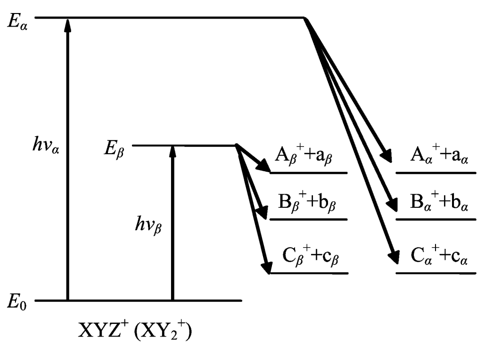

FIG. 1 Schematic energy level diagram of XYZ^+ (XY_2^+) related to their excitations and dissociations. There are two excitation-dissociation channels of α and β for XYZ^+ (XY_2^+).

much faster than the excitation rates, the production rates of fragments will depend dominantly on the excitation rates. We can write the observed total yields of fragmental ions as $[A^+]=[A_\alpha{}^+]+[A_\beta{}^+]$, $[B^+]=[B_\alpha{}^+]+[B_\beta{}^+]$, and $[C^+]=[C_\alpha{}^+]+[C_\beta{}^+]$.

We define the total fragment ions ratios as

$$R^{BA} = \frac{[B^+]}{[A^+]} = \frac{[B_\alpha{}^+]+[B_\beta{}^+]}{[A_\alpha{}^+]+[A_\beta{}^+]} \tag{3}$$

$$R^{CA} = \frac{[C^+]}{[A^+]} = \frac{[C_\alpha{}^+]+[C_\beta{}^+]}{[A_\alpha{}^+]+[A_\beta{}^+]} \tag{4}$$

Generally speaking, R^{BA} and R^{CA} are different from each other, and depend on the excitation laser intensity ratio $R_I=I_\alpha/I_\beta$. Hence we can study the competition of two excitation-dissociation channels by using the dependence of the total fragment ions ratios, R^{BA} and R^{CA} on the excitation laser intensity ratio $R_I=I_\alpha/I_\beta$ of α and β channels.

Based on the principle of vertical transition between two electronic states of molecules, it is known that the positions at the upper potential energy surface reached by the excitations of the α and β channels are determined by the Franck-Condon factor. That is, when the excitation laser wavelength is given, the position reached on the upper potential energy surface is also given. Accordingly the branching ratios of the ionic products will be constants at the given excitation laser frequencies.

$$r_\alpha^{BA} = \frac{[B_\alpha{}^+]}{[A_\alpha{}^+]}, \quad r_\alpha^{CA} = \frac{[C_\alpha{}^+]}{[A_\alpha{}^+]} \tag{5}$$

$$r_\beta^{BA} = \frac{[B_\beta{}^+]}{[A_\beta{}^+]}, \quad r_\beta^{CA} = \frac{[C_\beta{}^+]}{[A_\beta{}^+]} \tag{6}$$

Combining Eqs.(5) and (6) with Eqs.(3) and (4), we get

$$R^{BA} = \frac{r_\alpha^{BA}[A_\alpha{}^+]+r_\beta^{BA}[A_\beta{}^+]}{[A_\alpha{}^+]+[A_\beta{}^+]} \tag{7}$$

$$R^{CA} = \frac{r_\alpha^{CA}[A_\alpha{}^+]+r_\beta^{CA}[A_\beta{}^+]}{[A_\alpha{}^+]+[A_\beta{}^+]} \tag{8}$$

We define the total ion population density related to the α and β excitation channels as N_α and N_β, respectively. Their ratio is

$$\frac{N_\alpha}{N_\beta} = \frac{[A_\alpha{}^+]+[B_\alpha{}^+]+[C_\alpha{}^+]}{[A_\beta{}^+]+[B_\beta{}^+]+[C_\beta{}^+]} = \frac{[A_\alpha{}^+](1+r_\alpha^{BA}+r_\alpha^{CA})}{[A_\beta{}^+](1+r_\beta^{BA}+r_\beta^{CA})} = \frac{[A_\alpha{}^+]}{[A_\beta{}^+]}\xi^{-1} \tag{9}$$

$$\xi = \frac{1+r_\beta^{BA}+r_\beta^{CA}}{1+r_\alpha^{BA}+r_\alpha^{CA}} \tag{10}$$

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In fact, ξ deduced from $r_\alpha^{\rm BA}$, $r_\alpha^{\rm CA}$, $r_\beta^{\rm BA}$, and $r_\beta^{\rm CA}$ is also constant for the given laser frequencies ν_α and ν_β.

On the other hand, it is known that

$$\frac{N_\alpha}{N_\beta}=\frac{W_\alpha}{W_\beta}=\frac{\sigma_\alpha I_\alpha}{\sigma_\beta I_\beta}=R_\sigma R_I \tag{11}$$

Combining Eq.(9) and Eq.(11), we have

$$\frac{[{\rm A_\alpha}^+]}{[{\rm A_\beta}^+]} = \xi R_\sigma R_I \tag{12}$$

$$[{\rm A_\alpha}^+] = \xi R_\sigma R_I [{\rm A_\beta}^+] \tag{13}$$

Substituting Eqs.(12) and (13) in Eqs.(7) and (8), we get

$$R^{\rm BA} = \frac{[{\rm A_\beta}^+](r_\beta^{\rm BA}+r_\alpha^{\rm BA}\xi R_\sigma R_I)}{[{\rm A_\beta}^+](1+\xi R_\sigma R_I)} = \frac{r_\beta^{\rm BA}+r_\alpha^{\rm BA}\xi R_\sigma R_I}{1+\xi R_\sigma R_I} \tag{14}$$

$$R^{\rm CA} = \frac{r_\beta^{\rm CA}+r_\alpha^{\rm CA}\xi R_\sigma R_I}{1+\xi R_\sigma R_I} \tag{15}$$

In fact, when the two channels of α and β are excited simultaneously, the total fragment ions ratios $R^{\rm BA}$ and $R^{\rm CA}$ can be measured in experiment. The Eqs.(14) and (15) determine the function relations of $R^{\rm BA}$-R_I and $R^{\rm CA}$-R_I. Using Eqs.(14) and (15) to fit the measured $R^{\rm BA}$-R_I and $R^{\rm CA}$-R_I data, the "combined" parameters of ξR_σ, $r_\alpha^{\rm BA}\xi R_\sigma$, $r_\alpha^{\rm CA}\xi R_\sigma$, and "individual" parameters of $r_\beta^{\rm BA}$ and $r_\beta^{\rm CA}$ can be obtained. The individual parameters of $r_\alpha^{\rm BA}$, $r_\alpha^{\rm CA}$, and R_σ can be deduced from the fitted values of ξR_σ, $r_\alpha^{\rm BA}\xi R_\sigma$, $r_\alpha^{\rm CA}\xi R_\sigma$, then ξ can be determined by the Eq.(10). Finally, the excitation cross section ratio R_σ can be deduced from the ξ value and the fitted ξR_σ value.

III. DISCUSSION

A. Only one excitation channel is active

Consider the case that only one excitation channel is active. For example, turning off the dissociation laser of the α channel we have I_α=0 and R_I=0. That is, only the β excitation-dissociation channel is active. Substituting R_I=0 in Eq.(14) and Eq.(15), we get

$$R_0^{\rm BA}=r_\beta^{\rm BA}=\frac{[{\rm B_\alpha}^+]}{[{\rm A_\alpha}^+]} \tag{16}$$

$$R_0^{\rm CA}=r_\beta^{\rm CA}=\frac{[{\rm C_\alpha}^+]}{[{\rm A_\alpha}^+]} \tag{17}$$

Obviously, the obtained $R_0^{\rm BA}$=$r_\beta^{\rm BA}$ and $R_0^{\rm CA}$=$r_\beta^{\rm CA}$ values do not depend on the laser intensity and they are only related to laser wavelength, and $\rm XYZ^+$ ($\rm {XY_2}^+$) to be studied. It is worth noticing that the obtained $r_\beta^{\rm BA}$ and $r_\beta^{\rm CA}$ values in this case may differ slightly from the values fitted when two excitation channels are both active, but this is just a different choice for the initial parameter values.

B. Only two kinds of fragmental ions are produced in the dissociations of $\rm XYZ^+$ ($\rm {XY_2}^+$)

In the case that only two kinds of fragmental ions are produced in the dissociations of $\rm XYZ^+$ ($\rm {XY_2}^+$), supposing [A$^+$]≠0, [B$^+$]≠0, and [C$^+$]=0, then we have $r_\alpha^{\rm CA}$=0, $r_\beta^{\rm CA}$=0, $R^{\rm CA}$=0, and

$$R^{\rm BA}=\frac{r_\beta^{\rm BA}+r_\alpha^{\rm BA}\xi^a R_\sigma R_I}{1+\xi^a R_\sigma R_I} \tag{18}$$

with ξ simplified as

$$\xi^a=\frac{1+r_\beta^{\rm BA}}{1+r_\alpha^{\rm BA}} \tag{19}$$

By using Eq.(18) to fit the $R^{\rm BA}$-R_I data obtained in experiment, we can get parameters of $r_\beta^{\rm BA}$, $\xi^a R_\sigma$, and $\xi^a R_\sigma r_\alpha^{\rm BA}$. It is easy to get $r_\alpha^{\rm BA}$ from the fitted $\xi^a R_\sigma$ and $\xi^a R_\sigma r_\alpha^{\rm BA}$ values. Substituting the obtained $r_\beta^{\rm BA}$ and $r_\alpha^{\rm BA}$ values in Eq.(19), we get the ξ^a value. Finally, the R_σ value can be deduced from the ξ^a and $\xi^a R_\sigma$ values.

The typical example of this case was shown in Ref.[1] on the competition between $\tilde{H}\leftarrow\tilde{B}^2\Sigma_{\rm u}^+$ and $\tilde{C}^2\Sigma_{\rm g}^+\leftarrow\tilde{B}^2\Sigma_{\rm u}^+$ excitation channels of $\rm {CS_2}^+$ with the fragmental ions $\rm CS^+$ and $\rm S^+$ in the resulting dissociations. It is interesting to note that in this example it is needed to excite $\rm {CS_2}^+$ from $\tilde{X}^2\Pi_{\rm g}$ to $\tilde{B}^2\Sigma_{\rm u}^+$, then the fragmental ions $\rm CS^+$ and $\rm S^+$ are produced by the $\tilde{H}\leftarrow\tilde{B}^2\Sigma_{\rm u}^+$ and $\tilde{C}^2\Sigma_{\rm g}^+\leftarrow\tilde{B}^2\Sigma_{\rm u}^+$ excitation-dissociations. Provided that the two $\tilde{H}\leftarrow\tilde{B}^2\Sigma_{\rm u}^+$ and $\tilde{C}^2\Sigma_{\rm g}^+\leftarrow\tilde{B}^2\Sigma_{\rm u}^+$ excitation channels of $\rm {CS_2}^+$ are independent of each other, the measured total fragmental ion yields are the simple sum of the individual fragmental ion yields of the two excitation channels, and the Eqs.(14)-(19) are valid.

C. One excitation-dissociation channel has three kinds of fragmental ions and another channel has two kinds of fragmental ions

On occasion, we need consider the case in which one excitation-dissociation channel has three kinds of fragmental ions and another channel has two kinds of fragmental ions. For example, the photon energy in one excitation channel is below the highest dissociation limit but beyond other two dissociation limits. Provided that the two excitation channels are independent of each other, this case can be treated as if there only are two

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TABLE I Wavelength λ, beam waist radium w, focal length f, and laser energy E of the laser parameters used in experiment.

	Wavelength/nm	Beam waist radium/mm	Focal length/cm	Laser energy/(mJ/pulse)
Ionization laser	λ_0=333.06	w_{00}=1.5	f_0=13.5	4.0
Dissociation laser 1	λ_1=289.77	w_{01}=2.0	f_1=32.0	0.035
Dissociation laser 2	λ_2=748.11, 756.48	w_{02}=2.0	f_2=13.5	0-0.387

kinds of fragmental ions in the dissociations and the exclusive fragmental ions related to the given excitation channel can be regarded as an independent kind of ion.

Supposing that the β excitation channel only leads to two kinds of fragmental ions, we have $[A_\beta{}^+]\neq0$, $[B_\beta{}^+]\neq0$, $[C_\beta{}^+]=0$, and $r_\beta^{CA}=0$. Substituting $r_\beta^{CA}=0$ in Eq.(10), the parameter ξ becomes

$$\xi^b=\frac{1+r_\beta^{BA}}{1+r_\alpha^{BA}+r_\alpha^{CA}} \tag{20}$$

and the branching ratio R^{BA} of fragmental ions is then replaced by

$$R^{BA}=\frac{r_\beta^{BA}+r_\alpha^{BA}\xi^bR_\sigma R_I}{1+\xi^bR_\sigma R_I} \tag{21}$$

Using Eq.(18) to fit the measured R^{BA}-R_I data in experiment, we can obtain r_β^{BA}, $r_\alpha^{BA}\xi^bR_\sigma$, and ξ^bR_σ values, and then using these values and Eq.(18) the r_α^{BA}, ξ^b, and R_σ value can be deduced.

D. More than three kinds of fragmental ions are produced in the dissociations of XYZ^+ ($XY_2{}^+$)

In the case that four or more kinds of fragmental ions are in the dissociations of XYZ^+ ($XY_2{}^+$), by using the same deduction process as that for three kinds of fragmental ions, we can obtained a theoretical formula with a form similar to Eq.(12), if only we redefine the ξ by including more parameters of r_α^{BA}, r_α^{CA}, r_α^{DA}, r_β^{BA}, r_β^{CA}, r_β^{DA}, etc. For example, in the case of four kinds of fragmental ions $[A^+]=[A_\alpha{}^+]+[A_\beta{}^+]$, $[B^+]=[B_\alpha{}^+]+[B_\beta{}^+]$, $[C^+]=[C_\alpha{}^+]+[C_\beta{}^+]$, and $[D^+]=[D_\alpha{}^+]+[D_\beta{}^+]$ produced in the two excitation-dissociation channels, we can deduce

$$R^{BA}=\frac{r_\beta^{BA}+r_\alpha^{BA}\xi^cR_\sigma R_I}{1+\xi^cR_\sigma R_I} \tag{22}$$

$$R^{CA}=\frac{r_\beta^{CA}+r_\alpha^{CA}\xi^cR_\sigma R_I}{1+\xi^cR_\sigma R_I} \tag{23}$$

$$R^{DA}=\frac{r_\beta^{DA}+r_\alpha^{DA}\xi^cR_\sigma R_I}{1+\xi^cR_\sigma R_I} \tag{24}$$

$$\xi=\frac{1+r_\beta^{BA}+r_\beta^{CA}+r_\beta^{DA}}{1+r_\alpha^{BA}+r_\alpha^{CA}+r_\alpha^{DA}} \tag{25}$$

IV. THE COMPETITION BETWEEN TWO EXCITATION-DISSOCIATION CHANNELS FOR $CO_2{}^+$

In this experiment, we have studied the competition between the excitation-dissociation channel via $\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions and that via $\widetilde{C}^2\Sigma_g^+(200,120)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions for $CO_2{}^+$, where $\widetilde{H}$ represents the higher state reached by the excitation from $\widetilde{B}^2\Sigma_u^+(000)$ with the first dissociation laser of 289.77 nm. The $CO_2{}^+$ were prepared by the [3+1] resonance-enhanced multiphoton ionization of CO_2 using the ionization laser of 333.06 nm. The first dissociation laser of 289.77 nm was used to excite and dissociate $CO_2{}^+$ via $\widetilde{B}^2\Sigma_u^+(000)\leftarrow\widetilde{X}^2\Pi_{g,1/2}^+(000)$ and $\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions. When the second dissociation laser of 748.11 and 756.48 nm is used to dissociate $CO_2{}^+$ via $\widetilde{C}^2\Sigma_g^+(200,120)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transition, two excitation-dissociation channels via $\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions and via $\widetilde{C}^2\Sigma_g^+(200,120)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions, can coexist and compete with each other. Table I gives the laser parameters used in the experiment.

When we fixed the intensity of the first dissociation laser (289.77 nm) and changed the intensity of second dissociation laser (748.11 and 756.48 nm), a set of $R(O^+/CO^+)$-R_I data are obtained, where $R(O^+/CO^+)=[O^+]/[CO^+]$ and $R_I=I_2/I_1$ are the product branching ratio and the intensities ratio of two dissociation lasers, respectively. In Fig.2 the fragment ions ratios $R(O^+/CO^+)$ *vs.* the intensity ratios $R_I=I_2/I_1$ of two dissociation lasers are shown for the $\widetilde{C}^2\Sigma_g^+(200)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ and $\widetilde{C}^2\Sigma_g^+(120)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions. Fitting the R-R_I data according to the Eq.(14), the parameters r_H (r_β^{BA}), r_C (r_α^{BA}), and ξ are deduced. The results are $\xi=0.046\pm0.010$, $r_C=0.124\pm0.003$, $r_H=0.052\pm0.004$ and $\xi=0.025\pm0.005$, $r_C=0.148\pm0.004$, $r_H=0.050\pm0.003$ for $\widetilde{C}^2\Sigma_g^+(200)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ and $\widetilde{C}^2\Sigma_g^+(120)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions, respectively. Substituting these values of r_H, r_C, and ξ into Eq.(21), the excitation cross section ratios of $\widetilde{C}^2\Sigma_g^+\leftarrow\widetilde{B}^2\Sigma_u^+$ and $\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+$ transitions are deduced as $R_{\sigma(200)}=\sigma_{C(200)}/\sigma_{H2}=0.038\pm0.011$ for the competition between $\widetilde{C}^2\Sigma_g^+(200)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ and $\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions, and $R_{\sigma(120)}=\sigma_{C(120)}/\sigma_{H1}$ $=0.028\pm0.006$ for the competition between $\widetilde{C}^2\Sigma_g^+(120)$ $\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ and $\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions. According to the deduced values of $R_{\sigma(200)}$ and $R_{\sigma(120)}$ it is indicated that the excitation cross sections for

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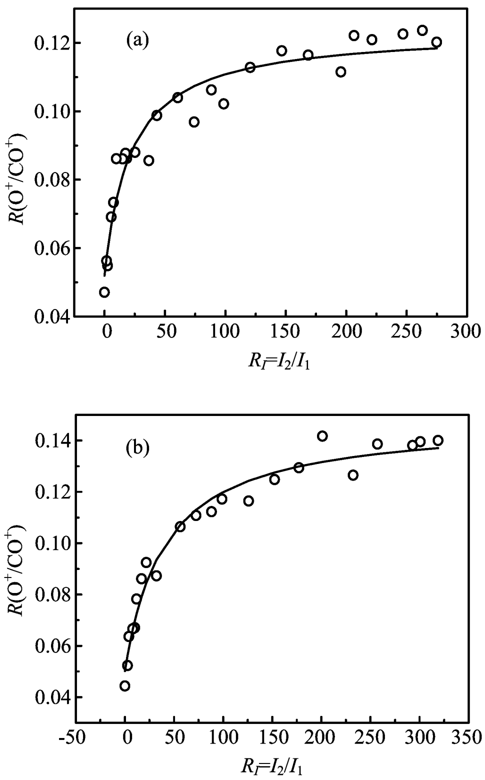

FIG. 2 Experimental (hollow circle) and theoretical (solid line) values of the product branching ratios $R(O^+/CO^+)$ versus intensity ratios $R_I=I_2/I_1$ of two beam intensities for the $\widetilde{C}^2\Sigma_g^+(200)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transition with the corresponding wavelength (λ_1=289.77 nm, λ_2=748.11 nm) (a) and $\widetilde{C}^2\Sigma_g^+(120)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transition with the corresponding wavelength (λ_1=289.77 nm, λ_2=756.48 nm) (b).

$\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions are much greater than the excitation cross sections for $\widetilde{C}^2\Sigma_g^+\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions.

V. CONCLUSION

We propose a theoretical model to study the competition of the two excitation-dissociation channels with more than two kinds of ionic products, such as A^+, B^+, and C^+, for XYZ^+ (XY_2^+). When the photo-excitation rates of two states E_α and E_β are much less than their dissociation or pre-dissociation rates, the deduced theoretical equations can be used to fit the measured data, which reflects the dependence of the product branching ratio on the intensity ratio of two excitation lasers. From the fitted parameters, the excitation cross section ratios of the two excitation-dissociation channels can be obtained. In experiment, the competition between the excitation-dissociation channels via $\widetilde{H}\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions and that via $\widetilde{C}^2\Sigma_g^+(200,120)\leftarrow\widetilde{B}^2\Sigma_u^+(000)$ transitions for ${CO_2}^+$ are studied. By measuring the dependence of the product branching ratio $R(O^+/CO^+)=[O^+]/[CO^+]$ on the intensities ratio $R_I=I_2/I_1$ of two dissociation lasers and fitting the experimental data with the theoretical equation, the excitation cross section ratios of $R_{\sigma(200)}=\sigma_{C(200)}/\sigma_{H1}=0.038\pm0.011$ and $R_{\sigma(120)}=\sigma_{C(120)}/\sigma_{H1}=0.028\pm0.006$ are deduced.

VI. ACKNOWLEDGMENT

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