

A MODEL STUDY OF LASER ISOTOPE SEPARATION BY PHOTOIONIZATION OR PHOTODISSOCIATION PROCESS

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Abstract

In this study, the selective photoexcitation of isotopic mixtures by laser light is investigated. Atomic and molecular methods are examined and rate equations are derived for both cases. Two and three step photoionization techniques are considered and rate equations are solved for ion yields. The molecular photodissociation process is also studied and the dependence of the dissociation product on the laser fluence is reported. The results of the developed model for SF_6 molecule is compared with the other results and the agreement found in this comparison indicates the validity of the developed model.

Introduction

Selective excitation and ionization by laser beam has found many applications in the field of laser spectroscopy [1]. One promising application using this method is the laser isotope separation and purification of materials at atomic or molecular level [2,3]. Selective atomic photoionization and molecular photodissociation can be used to produce highly pure substances in atomic states, alloys and molecular compounds [4,5]. Although there are other processes that can produce isotopes from a sample, with the advent of powerful tunable lasers, the laser technique has become more promising.

The selective photophysical processes have been developed for isotope separation which makes it possible to elaborate a new approach to materials technology and purification. Two and three photon stepwise excitation and photoionization are developed and reasonable models are given to characterise these processes. Another goal of this

study is to model selective photoexcitation and ultimate photodissociation of the polyatomic molecules. Photodissociation via one two step and multi step laser excitation are explained and multi photon dissociation is modeled for such molecules. The rate equations are solved and the effect of the laser fluence on product species is investigated.

Selective Photoionization of Atoms

Selective photoexcitation and subsequent photoionization (PI) of atoms is the most universal photophysical method for separation of products at atomic level. In the two step PI, the first photon at frequency, ω_1 selectively excites the atom and the second photon at frequency ω_2 is used to ionize the selectively excited atom in the sample. Similarly, three step method features the sequence of isotopically selective excitation and ionization of the excited atoms via three photons.

For the case of two photon ionization three coupled equations are involved:

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$$\dot{N}_0 = -W_{exc} (N_0 - N_1) + \frac{N_1}{\tau_{10}} \quad (1)$$

$$\dot{N}_1 = W_{exc} (N_0 - N_1) - w_{ion} N_1 - \frac{N_1}{\tau_{10}} \quad (2)$$

$$\dot{N}_i = W_{ion} N_1 \quad (3)$$

where N_0 defines the population density in the ground state, N_1 in the intermediate level 1, and N_i denotes the ion number density. The decay time of the level 1 considered to be τ_{10} which involves both the radiational and radiationless processes. Here W_{exc} is the excitation rate due to the first laser and W_{ion} is the ionization rate by the second laser.

For simplicity we define a_1 and a_2 as following:

$$a_1 = W_{exc} \left[1 + \frac{W_{ion} + 1/\tau_{10}}{2W_{exc}} \right] \quad (4)$$

$$a_2 = W_{exc} \left[1 + \frac{(W_{ion} + 1/\tau_{10})^2}{2W_{exc}} + \frac{1/\tau_{10}}{W_{exc}} \right]^{1/2} \quad (5)$$

where in the special case that excitation and ionization rates are much faster than the decay time τ_{10} , the decay term in equations (4) and (5) can be ignored.

The rate equations (1) - (3) are solved analytically and the result is:

$$\frac{N_1(t)}{N_a} = \frac{W_{exc}}{2a_2} [e^{-(a_1 - a_2)t} - e^{-(a_1 + a_2)t}] \quad (6)$$

$$\frac{N_i(t)}{N_a} = 1 - \frac{(a_1 + a_2)}{2a_2} e^{-(a_1 - a_2)t} + \frac{(a_1 + a_2)}{2a_2} e^{-(a_1 + a_2)t} \quad (7)$$

where the initial condition assumed to be $N_0(0) = N_a$, $N_1(0) = 0$ and $N_i(0) = 0$.

In the next study we have considered the three step process with photon frequencies, ω_1 , ω_2 and ω_3 . The number densities are N_0 , N_1 , N_2 for the ground state, level 1, level 2 and ion density is denoted by N_i . The decay time for level 1 and 2 are assumed to be τ_{10} , and τ_{20} and τ_{21} accordingly. The excitation rates are W_{exc1} , W_{exc2} , respectively and W_{ion} is the ionization rate by the third laser. The rate equations are given by:

$$\dot{N}_0 = -W_{exc1} (N_0 - N_1) + \frac{N_1}{\tau_{10}} + \frac{N_2}{\tau_{20}} \quad (8)$$

$$\dot{N}_1 = W_{exc1} (N_0 - N_1) - W_{exc2} (N_1 - N_2) - \frac{N_1}{\tau_{10}} + \frac{N_2}{\tau_{21}} \quad (9)$$

$$\dot{N}_2 = W_{exc2} (N_1 - N_2) - W_{ion} N_2 - \frac{N_2}{\tau_{21}} - \frac{N_2}{\tau_{20}} \quad (10)$$

$$\dot{N}_i = W_{ion} N_2 \quad (11)$$

These equations are solved numerically with the proper initial condition and the results are discussed in the following section.

Selective Photodissociation of Molecules

The photodissociation of molecules is possible through one-step, two-step (IR + UV) and multi-photon dissociator (MPD). Our intention is to study the MPD process in this article. This medium uses IR laser radiation for direct excitation of very high vibrational levels in the ground electronic state [6].

For molecules such as SF_6 , there are many thermally vibrational states, then we can assume lower discrete levels as well as quasi-continuum (QC) at higher energies. Three processes are distinguished to model IR excitation and collisionless dissociation [7]. At first, the molecule is excited from the vibrational ground state in a coherent multiphoton process in which 4 quanta are involved. This process is frequency dependent and therefore isotope selective. The second process occurs in the vibrational QC in which the molecule undergoes a sequence of one photon absorption and stimulated emission. Energy is rapidly exchanged with the other vibrational degrees of freedom through higher order anharmonic term.

An effective vibrational temperature may be introduced for this heating process. The same temperature may be used in the description of the dissociation in the third process.

Thus, the molecule in the statistical distribution with an energy exceeding the dissociation limit will dissociate at a rate given by the statistical kinetic theories of unimolecular reaction rates [8,9]. It is found that the thermal distribution is therefore a rather crude approximation of the real distribution created by laser excitation. This limits the validity of this model to cases with lower dissociation yields.

It has been shown [10] that the population distribution is always nonthermal and differs greatly from the results predicted by this simple model. Experimental results also indicated that the nature of the stepwise incoherent excitation and ultimate dissociation of the molecules depends on the properties of the QC.

Following the analysis given by Mitra [10], we have considered a model which takes both the fully coherent excitation in the lower discrete region and incoherent stepwise excitation in the QC into account with a coupling scheme that depends only on the time averaged population of the highest discrete level (ground state of the QC). In this model the anharmonic splitting of the degenerate v mode is taken into account and the effect of rotational levels is also considered. The effective field free molecular state defined by $|VLJR\rangle$, where V is the vibrational quantum number of the mode, L and J are the vibrational and total angular momentum quantum numbers respectively. The pure rotational angular momentum along the molecular axis is denoted by R [10].

If we define the fractional population C_n in the n -th

level of the QC, then we can write

$$\dot{C}_0 = -K_{01} P_3 C_0 + K_{10} C_1 \quad (12)$$

$$\dot{C}_1 = K_{10} P_3 C_0 - (K_{10} + K_{12}) C_1 + K_{21} C_2 \quad (13)$$

$$\dot{C}_n = K_{n-1,n} C_{n-1} - (K_{n,n-1} + K_{n,n+1} + X_n) C_n + K_{n+1,n} C_{n+1} \quad n \geq 2 \quad (14)$$

as (2a-2c) in Ref. [10]. Where $C_0 = C_0(t)$ is the total time dependent population of the discrete vibrational state and $C_0 P_3$ is the time dependent population of the ground state of the QC. Here P_3 depends on the laser frequency at different rotational temperatures and incorporates the anharmonic splitting of the v_3 mode. Parameter X_n is the dissociation rate from the level n . Coefficients $K_{n,n+1}^{(a)}$ and $K_{n+1,n}^{(e)}$ are given by [10]:

$$K_{n,n+1}^{(a)} = \frac{I}{h\nu} \frac{\sigma^{(0)} \gamma \sigma \gamma_n}{\gamma_n^2 + (\omega - \omega_0 + \alpha_n)^2} \left(1 + \frac{(n+s)(n-1)h\nu}{n+1}\right) \quad (15)$$

$$K_{n+1,n}^{(e)} = \frac{I}{h\nu} \frac{\sigma^{(0)} \gamma \sigma \gamma_n}{\gamma_n^2 + (\omega - \omega_0 + \alpha_n)^2} \left(1 + \frac{(n+s)(n-1)h\nu}{n+1}\right) \frac{(n+1)}{n+s} \quad (16)$$

where $(I/h\nu)$ is the photon flux, σ_n^* and σ_n^e are the absorption and emission cross sections, respectively. Here, s is the degree of freedom of the molecule and α_n is the anharmonicity factor for the level n .

The absorption cross section is defined such as is shown in Ref. [10], where n_R is the averaged quanta for the mode v_3 and d is vibrational dipole moment

$$\sigma_n^a = \frac{\sigma^{(0)} \gamma \sigma \gamma_n}{\gamma_n^2 + (\omega - \omega_0 + \alpha_n)^2} (1 + n_R) \quad (17)$$

as Equation (3) in Ref. [10] and with

$$\sigma^{(0)} = \frac{2\omega \langle d_{ij} \rangle^2}{3hc\gamma_0} \quad (18)$$

as Equation (4) in Ref. [10].

Here, α_n is the anharmonicity factor in the QC and γ_n is the laser linewidth defined by:

$$\gamma_n = \gamma_0 (1 + n)^a \quad (19)$$

where γ_0 and a are constants.

If we assume that there are m (molecules) and dissociation occurs at $n=33$ (see Ref. 10) of the QC, then we have:

$$W_d = 1 - \sum_{n=0}^{33} C_n(\tau) \quad (20)$$

which gives dissociation during pulsetime. The post pulse dissociation rate can be written as:

$$W_a = 1 - \sum_{n=N_1}^{\infty} C_n(\tau) \quad (21)$$

where N_1 is the dissociation threshold level assumed to be equal to 33.

The total molecules that can be dissociated is then given by:

$$W = W_d + W_a$$

$$W = 1 - \sum_{n=0}^{N_1-1} C_n(\tau) \quad (22)$$

The sets of equations given by (12) - (14) can be solved in order to find C_n and as result, W . This stochastic model gives a more accurate result in comparison with the simple model discussed before. Here, we do not need to consider collisions but the effect of collisions on the coherent multiphoton excitation of SF_6 in the lower discrete region of the v_3 mode has been studied recently [11]. By using the quantum Monte Carlo method they have calculated the effect of collisions of SF_6 with argon buffer and total leakage to QC of SF_6 during a pulse duration of about 100 ns has been reported.

Computations and Results

For the atomic case based on equations (1)- (3), a computer program is written to compute the state and ionization densities as a function of time. To normalize densities we have divided each population density to the ground state population density at zero time, N_0 . For the assumed value of $N_0 = 10 \times 10^{14} \text{ cm}^{-3}$, the normalized population densities as well as the ion density N_i/N_0 are plotted in Figure 1 for a time scale of about 1 ns. The

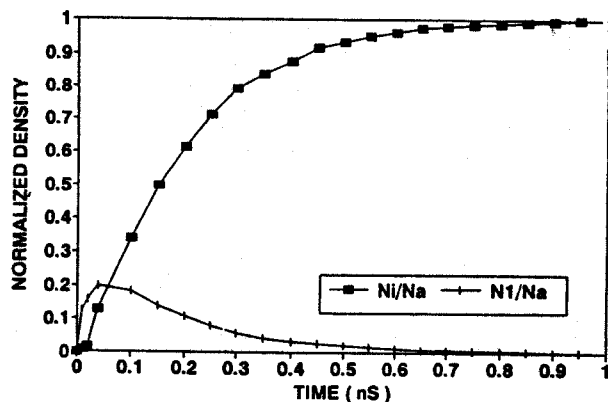


Figure 1. Variation of the normalized ion density, N_i/Na , and intermediate population density, N_1/Na , as a function of time for the two-step photoionization

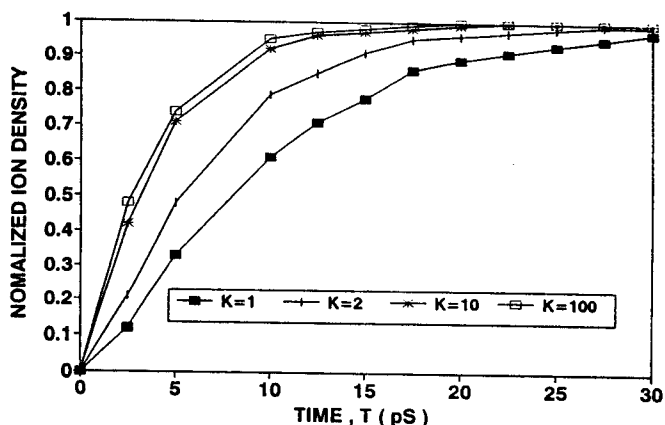


Figure 2. Variation of the normalized ion density for different K values as a function of time for two-step PI

simultaneous population of Ni and N1 are shown in Figure 1 for a better comparison. Results shown in Figure 1 indicate that during a time scale of about 1 ns, the ratio N_1/N_0 grows exponentially and reaches near unity. The rate of increase for the intermediate state N_1 is however faster than N_0 and reaches a maximum at a time of about 40 ps and decays to near zero value exponentially. The depletion of the ground population N_0 is also exponentially reaches near zero at a time duration of about 1 ns.

Figure 2 shows the variation of the normalized ion density as a function of time for the different laser excitation (P_{exc}) and ionization (p_{ion}) powers. As can be seen in Figure 2, this ratio is defined by $K=P_{ion}/P_{exc}$, and is plotted for the values of $K=1, 2, 10, \text{ and } 100$. Two major points can be drawn from this study. First, the ionization density grows exponentially while the rate of ionization is increased by increasing the K value. Second, it is noticed that the ionization rate increases from $K=10$ to 100 is not considerable, which suggests that the optimum K value is between 2 to 10 and spending more ionization power is not worth such a slight increase. The overall result of this part is that two photon ionization is a fast and effective method, in particular $K=2-10$ provides an optimum condition.

Based on rate equations (8-11), a program was written in basic to calculate and draw the state and ionization density for the three-step PI. The result is shown in Figure 3 and for a better comparison, this result is checked against the two-step PI. This comparison indicates that the two-step PI is a faster process and offers a higher ionization rate. It is therefore suggested that the two step process is the superior one and results in higher ion production with the same experimental conditions. For atoms with high ionization potentials, however, it is hard to accomplish two-step PI, so we are forced to use three-step PI.

In the case of MPD we have considered the SF molecule as a good candidate for our modeling molecule. Here it is assumed that the fundamental vibrational mod v_3 of the molecule is excited by the CO_2 laser pulse at $10.6\mu m$. It is also assumed that there are 4 discrete vibrational states and $3v_3$ is overlapping with the ground state of the QC which is defined by $n=0$. As discussed before, the dissociation threshold corresponds to $n=33$ in this MPD model. To solve the rate equations, first we need to calculate $K_{n+1,n}$ in Equations (15) (16). For these coefficients, we have $\omega_0=948\text{ cm}^{-1}$ and it has been assumed that $\alpha=3\text{ cm}^{-1}$, $\gamma_0=0.1414\text{ cm}^{-1}$, and $d_{01}=0.437D$

The dissociation fraction W is then computed by computer program and its logarithm is plotted as a function of the laser fluence, F, for different related parameters. In the first study, the role of the absorption cross section has been investigated and the results are shown in Figure 4. Here, the effect of the absorption cross section in the dissociation rate is shown which indicates that the dissociation product increases by increasing the laser fluence and its rate is mostly controlled by the absorptive cross section variation of the absorption cross section by a factor of 2 increases the dissociation fraction considerably.

In the next study, the effect of the line shape factor a on the absorption cross section as a function of the QC state number n is studied. The result of this study shows that the ratio $\sigma_n/\sigma^{(0)}$ is affected by a and its variation for $a=1$ and is displayed accordingly (see Figure 5). In another study, the effect of the laser pulse time τ , on the dissociation process is investigated and the results are shown in Figure 6.

For the final analysis, in Figure 7, we compare the results

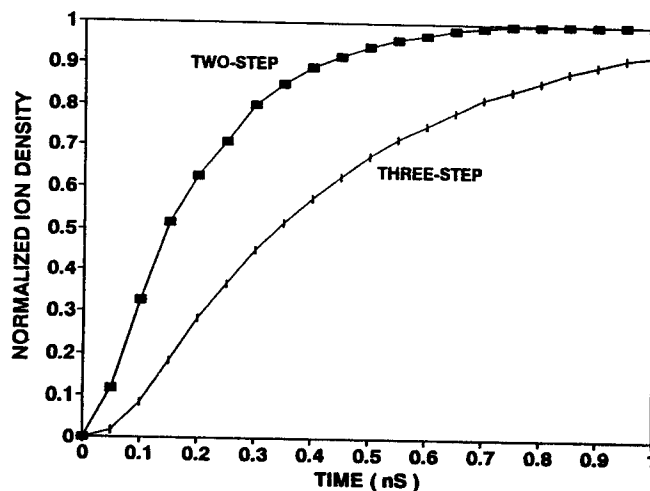


Figure 3. Comparison of the ion production for the two-step and three-step PI processes

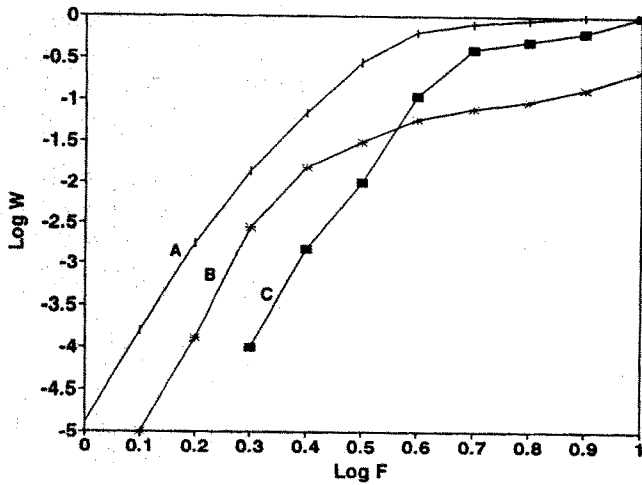


Figure 4. Variation of the dissociation product of SF_6 molecule as a function of laser fluence, F , for different absorption cross section values, $A = 2 \times 10^{-16} \text{ cm}^2$, $B = 3 \times 10^{-16} \text{ cm}^2$ and $C = 4 \times 10^{-16} \text{ cm}^2$

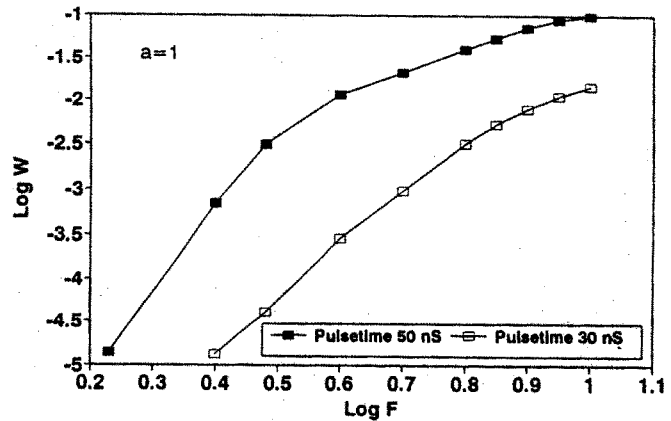


Figure 6. The effect of the laser pulsetime on the dissociation product as a function of the laser fluence in the MPD process

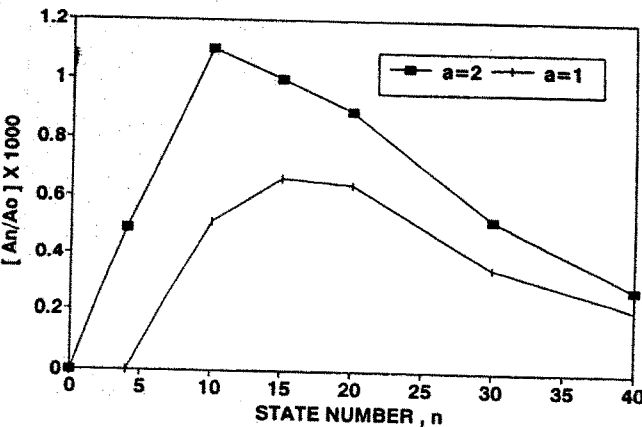


Figure 5. The effect of the line shape factor a , on the absorption cross section for different state numbers. Here, symbol A stands for the cross section

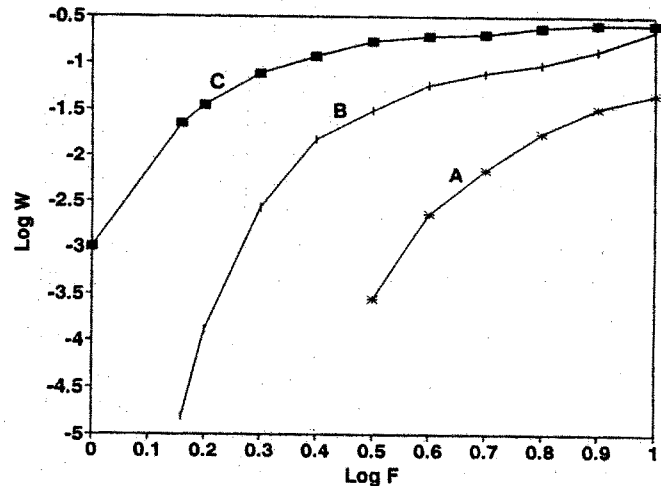


Figure 7. The effect of the line shape factor, a , on the dissociation fractions. Curve C shows our results computed for $a=2.0$. Curves A and B corresponding to $a=2.5$ and $a=2$, respectively are from (Ref. 12)

of this study with the experimental results given by Kolodner [12]. For this case, we assume $\gamma_0 = 0.1414$, $\alpha = 3.0$, $\omega_0 = 944.2 \text{ cm}^{-1}$ and curves marked as A, B and C are corresponding to values of $a=2.5$ and $a=2.0$. For this case we have compared our results curve C with the one given for $a=2$ (curve B) which shows good agreement.

Also we have compared our results with that reported in (Ref. 13), for different a values. The experimental results are based on the values $\tau = 100 \text{ ns}$, $\omega_0 = 944.2 \text{ cm}^{-1}$ and σ value of $3 \times 10^{-16} \text{ cm}^2$. In our calculation we see that the

results agree well for the case corresponding to the σ value of $3 \times 10^{-16} \text{ cm}^2$ which is shown in Figure 8.

Conclusion

The goal of this study has been twofold: (1) To model selective photoionization of atoms and compute the ion yields, and (2) to develop a simple computational model for molecular photodissociation. For the atomic case, the rate equations were developed and solved in order to obtain ionization products. The variation of ions as a function of

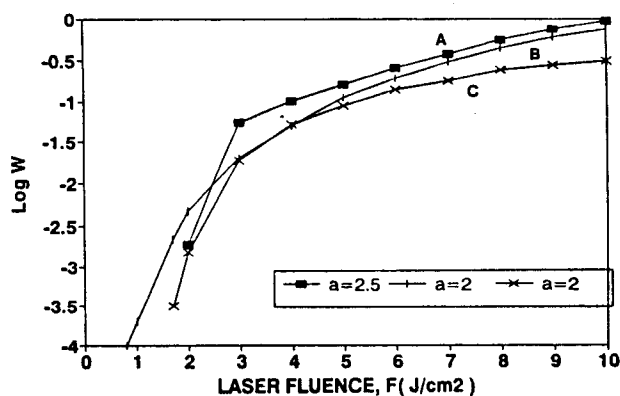


Figure 8. Comparison of the dissociation fraction obtained in this work (curve B for $\sigma = 3 \times 10^{-16} \text{ cm}^2$), with that of (Ref. 13) Curve A corresponds to $\sigma = 4 \times 10^{-16} \text{ cm}^2$ and curve C corresponds to $\sigma = 3 \times 10^{-16} \text{ cm}^2$

time for different laser parameters has been investigated. The result suggests that two-step PI provides higher ion yields so they should be equipped for possible cases.

For the molecular case, a simple model was developed which interfaces discrete level to the QC to explain the dissociation rate. The fraction of the dissociated molecules depends on the laser parameters (fluence, pulsetime, and linewidth) and the characteristics of the QC (absorption cross section and dissociation rate). The model reported nicely describes the photodissociation of the SF_6 by multiphoton pulses of CO_2 laser. The dissociation fraction derived from our calculations is checked against other results and the obtained results agree. The overall conclusion is that the models given in this report are simple and accurate to explain laser isotope PI and MPD processes.

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