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Isotopic Selectivity of IR Laser Photodissociation of CF_3I Molecules

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Abstract. The selectivity dependence of multiphoton dissociation of CF_3I on the conditions of excitation (pulse duration, concentration of the isotope under excitation and gas pressure) has been studied. It has been shown that the main mechanism of selectivity loss is $V-V$ exchange during a laser pulse. The elaborated model is in good agreement with the experiment.

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Isotopic selectivity of dissociation of polyatomic molecules by ir laser radiation is one of the most important characteristics of this phenomenon when it is especially applied in isotope separation [1]. Such basic parameters of isotope separation by laser as efficiency and energy consumption are substantially dependent on the selectivity value, and hence an essential condition for creating an efficient process of industrial scale [2, 3] isotope separation is to obtain a maximum of selectivity value.

The purpose of this work was to carry out studies to ascertain the mechanism of selectivity loss using the CF_3I molecule as an example. Some experiments have been performed to study how the selectivity of dissociation of $^{12}CF_3I$ and $^{13}CF_3I$ molecules depends on the excitation conditions such as gas pressure and temperature, laser pulse length. A fairly simple model has been elaborated which is in good agreement with our experiment. The studies are of interest not only from the viewpoint of their practicability in isotope separation but also provide important information on the processes taking place in molecular gas being excited by an ir radiation pulse.

1. Experiment

CF_3I used in our experiments had the natural content of isotopes ^{13}C ($x_0=0.0108$) and ^{12}C ($1-x_0=0.9892$). The absorption bands of $^{13}CF_3I$ and $^{12}CF_3I$ of the ν_1 mode occur within the limits of the CO_2 laser radiation frequency in the band 00°1→02°0, with the isotope shift in this vibration $\Delta\nu=26.5\pm1\,\mathrm{cm}^{-1}$ [4]. The content of CF_3I in the gas was no less than 99.9%.

The dissociation of CF_3I molecules was done by TEA CO_2 laser radiation. The shape of the laser pulse used is given in Fig. 1. The "short" pulse in the front peak had $y_0=0.75$ of the total pulse energy, the "long" one had $y_0=0.35$. All the experiments were conducted in a cell made of stainless steel of 14 mm diameter with a nonfocused laser beam 8 mm diameter. As shown in [5], the dissociation of CF_3I occurs with breaking a C–I bond, and the final product of dissociation is C_2F_6. The characteristics of excitation and dissociation of CF_3I molecules have been investigated in more detail in [4, 6].

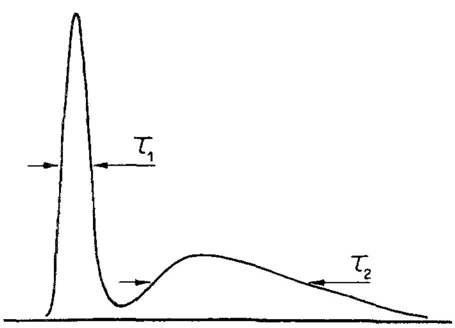

Fig. 1. Pulse of CO_2 laser. 1 Short pulse: $\tau_1=8\cdot10^{-8}$ s, $\tau_2=5\cdot10^{-7}$ s, $y_0=0.75$, $\tau_s=1.85\cdot10^{-7}$ s. 2 Long pulse: $\tau_1=8\cdot10^{-8}$ s, $\tau_2=1.15\cdot10^{-6}$ s, $y_0=0.35$, $\tau_L=7.75\cdot10^{-7}$ s

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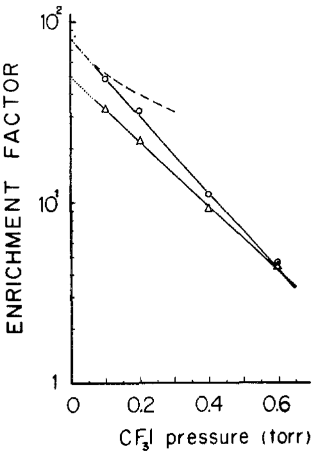

Fig. 2a. Dependence of enrichment factor on pressure with $^{12}CF_3I$ under excitation [*R*(14) line of CO_2 laser]. Upper curve: $T = -45\,°C$. Lower curve: $T = +20\,°C$. Dashed line: calculation by the model

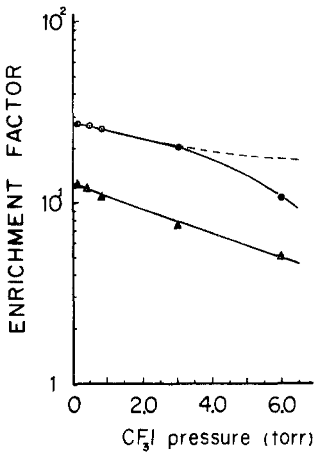

Fig. 2b. Dependence of enrichment factor on pressure with $^{13}CF_3I$ under excitation [*R*(26) line of CO_2-laser]. Upper curve: $T = -45\,°C$. Lower curve: $T = +20\,°C$. Dashed line: calculation by the model

Dissociation selectivity α is determined by the ratio of dissociation yield β of isotope under excitation to that of unexcited. With $\beta \Gamma N < 1$, where Γ is the ratio of irradiated volume to total cell volume, N is the number of pulses, α is equal to the enrichment factor Q. This value was measured by a mass spectrometer from $C_2F_5^+$ ions

$$Q = \left[\frac{2x_0}{1-x_0} \cdot \frac{[^{12}C^{12}CF_5^+]}{[^{13}C^{12}CF_5^+]} \right]^n , \qquad (1)$$

where $n = 1$ with $^{12}CF_3I$ excited, and $n = -1$ with $^{13}CF_3I$ excited.

Figure 2 shows the Q dependence on the total gas pressure p when both $^{12}CF_3I$ (a) and $^{13}CF_3I$ (b) are excited. The experiments were performed at room temperature ($+20\,°C$) and on cooling to $-45\,°C$. Measurements were taken with a "short" pulse and the energy fluence of $1.3\,j/cm^2$, thus the dissociation yield $^i\beta = 0.25$ [4] with no more than 50% of $^iCF_3I$ dissociated in the whole cell volume (where $i = 12$ or 13). As may be seen, all the measured curves can be presented, at least at the initial section, by an expression like $Q = Q_0 \exp(-p/p_0)$, where Q_0 is the maximum value of enrichment factor when $p \to 0$ and p_0 is a pressure at which Q decreases by factor e. The measured values of Q_0 and p_0 are given in Table 1.

The obtained results show that as both $^{12}CF_3I$ and $^{13}CF_3I$ are excited the value of enrichment factor increases with gas cooling, and the less the gas pressure the higher this increase. Yet the most essential feature of the curves in Fig. 2a and b is that the dependence of

Table 1. Parameters of isotope selectivity of CF_3I dissociation

	Excitation of $^{13}CF_3I$		Excitation of $^{12}CF_3I$	
	$+20\,°C$	$-45\,°C$	$+20\,°C$	$-45\,°C$
Q_0	12.6	28	50	80
$\mathbf{p}_0$ [Torr]	6.4 ± 0.1	10.6 ± 0.1	0.24 ± 0.005	0.20 ± 0.005
$\mathbf{k}_0$ [$s^{-1}\,Torr^{-1}$]	$2.44 \cdot 10^6$	$1.22 \cdot 10^6$	$1.38 \cdot 10^6$	$1.03 \cdot 10^6$

Table 2. Dependence of selectivity on laser pulse length

	Excitation of $^{13}CF_3I$		Excitation of $^{12}CF_3I$	
	$p = 0.8$ Torr Experiment	$T = -45\,°C$ Model	$p = 0.2$ Torr Experiment	$T = 20\,°C$ Model
Short pulse	25.3	25.9	21,8	27.3
Long pulse	17.9	19.8	10.2	11.2
Ratio	1.41	1.31	2.14	2.44

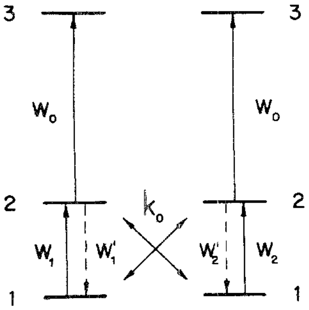

Fig. 3. Model of CF_3I excitation

Q on total gas pressure in the case of $^{13}CF_3I$ excitation is weaker than that in the case with $^{12}CF_3I$. It must be said, also, that the value of the enrichment factor when $^{13}CF_3I$ is excitated remains high even at comparatively high gas pressures ($Q = 20$ when $p = 3$ Torr).

Also, we measured the value of enrichment factor Q for different pulses, short and long ones, the energy fluence being equal 1.3 j/cm^2. The experiments were performed with both $^{13}CF_3I$ and $^{12}CF_3I$ excited. (The radiation pulse frequency was the same as it is in Fig. 2a and b.) The results of the measurements are given in Table 2 from which one can see that an increase in the pulse length causes the selectivity of molecular dissociation to fall.

2. Model

To explain the experimental results we used the following fairly simple model. It was expected that a decrease in selectivity resulted in energy exchange in collisions between molecules with various isotopes throughout the laser pulse. This process causes the molecules with an undesired isotope to gain an energy being sufficient for their excitation to vibrational quasicontinuum and subsequent dissociation by laser radiation.

Really, colliding molecules can be in every possible energy state and therefore the rate of energy exchange may depend on the level of molecular excitation. In our model the process of exchange and radiation excitation is being considered in a simplified way. The molecules excited to quasicontinuum may be considered as a single whole (state 2 in Fig. 3). and the interaction of these molecules with those at the lower levels (state 1 in Fig. 3) is described by one phenomenological rate constant k_0 of $V-V$ exchange. The excitation from state 1 to state 2 occurs at the rates W_1 and W_2. The rate of excitation to the energy range from which dissociation takes place (state 3 in Fig. 3) is equal to W_0. The value of W_0 is considered to be the same for the both isotopes.

This model corresponds to the division of the process of molecular excitation into two-stages [7]. At the first stage excitation occurs at several lower vibrational levels and can be isotopically selective. At the second one it takes place in the vibrational quasicontinuum. Due to a large spectral width of the quasicontinuum the cross sections of this process may be considered the same for the both isotopes.

The equations corresponding to the model under consideration (Fig. 3) take the forms

$$dm_1/dt = -W_1m_1 + W_1'm_2 - k_0m_1M_2 + k_0m_2M_1\,, \tag{2}$$

$$dm_2/dt = -W_0m_2 + W_1m_1 - W_1'm_2 - k_0m_2M_1 + k_0m_1M_2\,, \tag{3}$$

$$dM_1/dt = -W_2M_1 + W_2'M_2 - k_0m_2M_1 + k_0m_1M_2\,, \tag{4}$$

$$dM_2/dt = -W_0M_2 + W_2M_1 - W_2'M_2 - k_0m_1M_2 + k_0m_2M_1\,, \tag{5}$$

where m_1, m_2 and M_1, M_2 are the populations of states 1 and 2 for $^{13}CF_3I$ and $^{12}CF_3I$, respectively. The dissociation yield for each isotope can be determined as

$$\beta_1 = \frac{W_0}{m_1^0}\int_0^\tau m_2(t)dt\,,$$

$$\beta_2 = \frac{W_0}{M_1^0}\int_0^\tau M_2(t)dt\,, \tag{6}$$

where τ is the pulse length, m_1^0 and M_1^0 are the initial concentration of $^{13}CF_3I$ and $^{12}CF_3I$. To derive a solution from (2) to (5) in analytical form m_1 and M_1 were assumed to remain constant that corresponded to low dissociation yields[1]. Besides, the reverse transitions of W_1' and W_2' were disregarded (Fig. 3).

As a result, for selectivity α' ($^{13}CF_3I$ to be excited) we may have

$$\alpha' = \frac{\beta_1}{\beta_2} \simeq \frac{W_1(3-W_0\tau)-(1-x_0)(W_1-W_2)\tau k_0p}{W_2(3-W_0\tau)+x_0(W_1-W_2)\tau k_0p}\,, \tag{7}$$

where $p = m_1^0 + M_1^0$ is the total gas pressure. Expression (7) was derived on the additional assumptions that $1/2W_0\tau \ll 1$ and $1/2\tau k_0p \ll 1$. With $p \to 0$ we have the obvious result $\alpha' \to \frac{W_1}{W_2} \equiv \alpha_0'$, i.e., the ultimate selectivity α_0' is determined by the ratio of the radiation excitation rates W_1 and W_2. Finally we have that

$$\alpha' = \frac{\alpha_0'(3-W_0\tau)-(1-x_0)(\alpha_0'-1)\tau k_0p}{(3-W_0\tau)+x_0(\alpha_0'-1)\tau k_0p}\,. \tag{8}$$

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[1] Knowing the β value and the fraction of molecules remaining in the ground state [6] we can determine the values W_1, W_2, W_0 and solve (2)–(5) numerically. With $\beta = 0.25$ the found values for selectivity coincide with that for α'' from (8) accurately to several per cent with $p < p_0''$.

For the slope of dependence (8) we can attain

$$v_1 = \frac{1}{\alpha_0'} \frac{d\alpha'}{dp}\bigg|_{p=0} = -\frac{(\alpha_0'-1)[1+x_0(\alpha_0'-1)]\tau k_0}{\alpha_0'(3-W_0\tau)}. \tag{9}$$

In a like manner, we have for the excitation of $^{12}CF_3I$

$$\alpha'' = \frac{\beta_2}{\beta_1} = \frac{\alpha_0''(3-W_0\tau)-x_0(\alpha_0''-1)\tau k_0 p}{(3-W_0\tau)+(1-x_0)(\alpha_0''-1)\tau k_0 p}, \tag{10}$$

$$v_2 = \frac{1}{\alpha_0''} \frac{d\alpha''}{dp}\bigg|_{p=0} = -\frac{(1-x_0)(\alpha_0''-1)\tau k_0}{3-W_0\tau}, \tag{11}$$

where $\alpha_0'' = W_2/W_1$ is the ultimate dissociation selectivity, determined by spectral selectivity of excitation.

3. Comparison Between Model and Experiment

The first essential conclusion following from solution of (2)–(5) resides in the fact that the character of the selectivity-pressure relation may vary greatly as molecules with high and low isotope contents are excited. In the latter case, when $x_0 \ll 1$, the relation between α' and p is determined by the factor $\alpha_0' x_0$. When $\alpha_0' x_0 \gg 1$ the selectivity depends on the *partial pressure* of a rare isotope under excitation [viz. (8)] and by the *total gas pressure* when $\alpha_0' x_0 \ll 1$. Because of this, when the radiative selectivity is rather high the pressure dependence of selectivity may be much slower as a rare isotope is excited. This conclusion is in good agreement with experiment (Fig. 2a and b). Really, we have from (9) and (11) that

$$v_2/v_1 = \frac{(1-x_0)(\alpha_0''-1)\alpha_0'}{[1+x_0(\alpha_0''-1)](\alpha_0'-1)}. \tag{12}$$

(It should be noted that v_2/v_1 is determined only by the values of x_0, α_0', α_0'' and independent of the rates of radiation excitation and exchange.) Substituting the values of Q_0' and Q_0'' (we assume that $Q_0' = \alpha_0'$ and $Q_0'' = \alpha_0''$) into (12) we can get from Table 1 that with $T = -45\,°C$, for example, $v_2/v_1 = 62{,}7$ which is in good agreement with the experimental value $v_2/v_1 = p_0'/p_0'' = 53$.

The pulses of CO_2 laser radiation used in our experiments had a shape that differed from rectangular (Fig. 1). Our measurements show that the dissociation yield of CF_3I molecules in this experiment is conditioned by only pulse energy fluence and does not depend on pulse shape. Therefore, we may introduce the effective pulse length

$$\tau = y_0\tau_1 + (1-y_0)\tau_2, \tag{13}$$

where τ_1 and τ_2 denote the half-height width of the front peak of pulse and its "tail" (Fig. 1), and y_0 is the fraction of total pulse energy contained in the front peak. From (13) we have $\tau_s = 1.85 \cdot 10^{-7}$ s for short pulses and $\tau_L = 7.75 \cdot 10^{-7}$ s for long ones.

Knowing the experimental slope values for the pressure dependence of Q the Q' and Q'' values and the pulse length τ we can derive from (9) and (11) the value of the energy exchange rate constant k_0. The values of k_0 obtained for $T = +20\,°C$ and $T = 45\,°C$ are given in Table 1. We should note that the magnitudes of k_0 obtained in independent experiments on excitation of $^{13}CF_3I$ and $^{12}CF_3I$ are very close. The order of magnitude obtained for k_0 is $10^6\,s^{-1} \cdot Torr^{-1}$ that is of the same order with the typical value of the rate constant of $V-V$ exchange in polyatomic molecules. Using the above values of k_0 it is possible to calculate the dependence of α on p by (8) and (10). In Fig. 2a and b the results of such calculations for $T = -45\,°C$ are given by a dashed line. The discrepancy between experiment and calculation with $p > p_0$ is conditioned by two causes. First, the study of the process of excitation and exchange is simplified. Here, in particular, we do not take into account the changes in the average level of excitation of molecules with an undesired isotope during the process of $V = V$ exchange. Second, we do not consider here the dissociation of highly excited molecules by their collisions after the laser pulse is over. The contribution of this process may be essential at high gas pressures [8].

From expressions (8) and (10) we can also calculate the values of α' and α'' for various pulse lengths τ_s and τ_L assuming that the ultimate radiation selectivity α_0' and α_0'' is independent of τ. The results obtained for excitation of $^{13}CF_3I$ ($p = 0.8$ Torr) and $^{12}CF_3I$ ($p = 0.2$ Torr) are given in Table 2, where also the experimentally measured values of Q' and Q'' can be found. The comparison between experiment and calculations shows that in this case the model agrees well with the experiment, too. We wish to mention one more result following from the model. As it transpires from (11), when exciting a rich isotope the following condition should be met.

$$p_0''(\alpha_0''-1) = \text{const}. \tag{14}$$

Thus, changing α_0'' by frequency tuning, for example, we can change the rate of the α'' dependence on p. Therefore, proceeding from (14), it is possible to optimize the choice of radiation frequency and gas pressure in isotope separation. The experiments on $^{12}CF_3I$ with $T = -45\,°C$ and $T = +20\,°C$ confirm (14). It can be seen from Fig. 2a that a decrease of α_0'' with increasing T causes p_0'' to rise (Table 1). It is somewhat less here than it follows from (14) that may be due to the dependence of k_0 on T.

4. Conclusions

Thus, the above comparison shows that the elaborated model, despite its simplified character, well describes the experimentally observed dependence of Q on pressure (with $p<p_0$) and pulse length. Also it shows that the value of $\alpha_0 x_0$ is a criterion defining the character of the dependence of α on p as a rare isotope ($x_0 \ll 1$) is excited. This conclusion is also attested by experiments on dissociation of $^{33}SF_6$ [9]. Due to a small value of $\alpha_0 x_0 = 0.06$ in this case p_0 turned out to be approximately the same in value as it was in the case of $^{32}SF_6$ excitation.

A decrease in selectivity with increasing gas pressure occurred in the earliest experiments on dissociation of poly-atomic molecules [7]. It was proposed then that such a behavior might be caused by the process of $V-V$ exchange between different isotopic molecules. Yet it is possible to illustrate that the dependences of α on p similar to (8) and (10) can be obtained with another mechanism of selectivity loss, too, as well as in a bimolecular process. Selectivity can be lost even after a laser pulse from subsequent reactions like

$$^{12}CF_3I + {}^{13}CF_3 \leftrightarrows {}^{12}CF_3 + {}^{13}CF_3I\,. \qquad (15)$$

In works [10, 11] it has been proposed that process (15) is the main channel of selectivity loss during dissociation of CF_3I molecules. The evailable information on the rates of reactions like (15) indicates that the time reaction (15) under the conditions of our experiments must be several orders longer than the laser pulse length τ. And hence, there should not be such a strong dependence on τ as it can be experimentally observed, and it follows from the model elaborated in the present paper. This fact enables us to conclude that the process of $V-V$ exchange throughout the laser pulse is the main channel of radiation excitation selectivity loss in the case of CF_3I at least. The reasonable value attained for k_0, despite a simplified character of the model, favours this mechanism of selectivity loss. It is comparable with the known ones for the rate constants of $V-V$ exchange in such molecules. Thus, $V-V$ processes are fast enough to provide the observed decrease of selectivity throughout the laser pulse. We must note that the rate of this process is determined not only by k_0 but also varies directly with α_0, and (14) is a consequence of this.

At last we want to dwell on the maximum dissociation selectivity α_0. This value as seen from the above said governs, in many respects, the values of α at finite pressures. A strong temperature dependence of α_0 confirms the conclusion that it is determined by spectral selectivity of excitation and resulted in the radiative excitation of an undesired isotope at the wing of its multiphoton excitation band.

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