Isotope-selective photodissociation of CF_3I molecules in multiphoton vibrational excitation followed by electron excitation by laser radiation

I. N. Knyazev, Yu. A. Kudryavtsev, N. P. Kuz'mina, and V. S. Letokhov

Spectroscopy Institute, USSR Academy of Sciences

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We investigate the effect of vibrational excitation of CF_3I molecules by laser radiation. A sharp increase of the absorption is observed on the long-wave edge of the first UV absorption band. A model is proposed wherein the increase of the UV absorption explains satisfactorily the experimental results. Isotope-selective dissociation of CF_3I molecules is realized by a method of successive IR and UV excitation.

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1. INTRODUCTION

Methods for selective action of laser radiation on atoms and molecules, based principally on sequential multistep excitation of quantum states, are actively investigated at present (see, for example, the review by Letokhov[1]). Two approaches are successfully used for molecules: 1) excitation of electronic states via an intermediate vibrational state through joint action of infrared and ultraviolet laser radiation,[2] wherein the infrared radiation provides the selective vibration excitation, and the ultraviolet dissociates the already excited molecules[3]; 2) direct excitation of the high-lying vibrational states up to the dissociation limit[4] (the question of multiphoton dissociation of complex molecules is considered in detail in a review by Ambartsumyan and Letokhov[5]).

In the present paper we investigate an intermediate case, which consists of multiphoton vibrational excitation of molecules below the dissociation limit, followed by excitation into the electronic state. This approach is valuable, first, because the limit of ultraviolet absorption is appreciably shifted in the red direction, and consequently a higher selectivity of the isotope separation process is ensured; second, there is no need to excite molecules to the limit of the dissociation only by the infrared radiation, so that less powerful infrared sources can be used; third, there is a possibility of investigating the excitation of high-lying vibrational states, an important factor for the understanding of the kinetics of the process of multiphoton dissociation of molecules. This method was already used before in investigations of the vibrational excitation of the molecules OCS (Ref. 6) and O_sO_4,[7] and of the photoisomerization of trans-dichloroethylene.[8]

The present paper is devoted, first, to the study of ultraviolet absorption by a CF_3I molecule in the first electronic band when its vibrational levels are excited by radiation from a powerful infrared CO_2 laser and, second, to an investigation of carbon isotope separation by selective infrared-ultraviolet dissociation of CF_3I molecules by the joint action of the radiation of a CO_2 laser and XeCl and XeF excimer lasers.

The choice of the CF_3I molecule was dictated by the fact that the infrared absorption band ν_1 coincides with the generation frequencies of the CO_2 laser, and the isotopic shift amounts to 26 cm^{-1} (Refs. 9, 10). It is therefore possible to obtain effective isotopically selective excitation of $^{12}CF_3I$ and $^{13}CF_3I$ molecules. Nonselective dissociation of unexcited (thermally excited) CF_3I molecules irradiated in the first ultraviolet absorption band has been relatively well investigated,[11] since these molecules are used in active media of atomic-iodine lasers, and the generation frequencies of the excimer lasers (XeF, XeCl) lie on the long-wave edge of the absorption band.[1)]

2. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1. The vibrational levels of the CF_3I molecules were excited by a TEA CO_2 laser 1. The radiation pulse energy was 0.8 J, and the duration was 70 nsec at half-maximum. The "tail" of the laser pulse contained not more than 20% of the energy, and the active medium consisted of CO_2:N_2:He in a ratio 4:1:16. Discrete tuning of the frequency of the CO_2 was produced with a diffraction grating 2. The radiation was reflected by mirrors 3 and 4 to a cell with gas 14. The attenuation of the radiation was by means of calibrated attenuators 5.

The opposite side of the cell was irradiated with ultraviolet lasers 13 (XeF, N_2, or XeCl). The excimer lasers were similar in construction to that described in Ref. 4. The XeCl and XeF laser pulse energy was 50 mJ, the duration was 25 nsec at half-maximum. The XeCl laser used the mixture HCl:Xe:He = 1:15:600. The working mixture of the XeF laser was NF_3:Xe:He = 1:4:600. The nitrogen laser pulse energy was 2 mJ.

An important problem in the case of stepwise infrared-ultraviolet excitation of molecules is the proper synchronization of the laser radiation pulse. The time synchronization of the pulses of CO_2 and ultraviolet lasers was effected using a coaxial cable in the circuit that triggered the ultraviolet laser by a voltage pulse produced on the cell of the CO_2 laser. The CO_2 laser pulse led the ultraviolet laser pulse by a time τ_3, which was regulated by the length of the cable and by the pressure in the trigatron discharge gap in the supply circuit of the ultraviolet laser. The synchronization was accurate to

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±10 nsec. The synchronization of the infrared and ultraviolet pulses was monitored by reflecting part of the radiation from the plates to a receiver based on carrier dragging by the photons and to a coaxial photocell. The registration was by means of an S8-7 oscilloscope.

To measure the ultraviolet absorption, a diaphragm 10 of 1 mm diameter was used to separate the central part of the radiation, which was directed coaxially with the CO_2-laser radiation to a cell with CF_2I. The windows of the cell were tilted at an angle 45°. Part of the radiation at the entrance and exit of the cell was directed to photocells 9 and 7. The signals from the photocells were fed to the differential amplifier of the S8-2 oscilloscope. The equalization of the signals from the photocells in the absence of absorption was produced by an attenuator located ahead of photocell 9. Thermopiles and microvoltmeters F-116/2 were used to measure the absorption of the infrared radiation. The cell was 0.92 m long and was made of glass, and the windows were plates of CaF_2 which passed the radiation of both the CO_2 laser and of the excimer lasers. Prior to the filling with CF_3I, the cell was evacuated by an absorption pump to a pressure 10^{-3} Torr. The absorption measurements were made at pressures from 0.1 to 1 Torr.

In the experiments on isotopically selective dissociation, the diaphragm 10 was removed and the entire radiation of the excimer (XeF or XeCl) laser was focused by a lens of focal length $f = 0.5$ m into a cell with CF_3I, 16 cm long and with volume $V = 16$ cm^3. To decrease the dissociation of the CF_3I by the CO_2 laser radiation alone, the aperture of the infrared radiation was equal to the aperture of the ultraviolet radiation at the entrance and exit of the cell. An analysis of the dissociation products and of the CF_3I production was based on the infrared absorption spectra in the region 2000–1000 cm^{-1}, using an IKS-24 spectrophotometer. The CF_3I dissociation was carried out both in pure gas and with an acceptor (oxygen) added. The pressure of the CF_3I in the cell was 0.2 Torr. The isotopic selectivity in the dissociation products was measured with an MI 1309 mass spectrometer. The measurements were made relative to the peaks $m/e = 119$ and 120 of the $C_2F_5^+$ fragment after irradiation of CF_3I without an acceptor. The ultraviolet absorption spectrum was measured with a Specord UV VIS spectrophotometer.

3. INVESTIGATION OF ULTRAVIOLET ABSORPTION OF THE CF_3I MOLECULE UNDER VIBRATIONAL ABSORPTION

A. Results of experiments

The absorption spectrum of the CF_3I molecules in the ultraviolet region of the spectrum is shown in Fig. 2a. The maximum of the first electron band is at 37 500 cm^{-1}. The absorption spectrum is continuous because the CF_3I molecules dissociate when they absorb light in this band. The arrows on the figure show the lasing frequencies of the excimer XeF and XeCl lasers and of the N_2 laser.

The absorption spectrum of the CF_3I molecule in the infrared region from 1000 to 1200 cm^{-1} is shown in Fig. 2b. The vibrational excitation was on the $R(14)$ line of the 9.3 μm band of the CO_2 laser. This frequency corresponds to the center of the Q branch of the valence oscillation of the ν_1 mode of the $^{12}CF_3I$ molecule. The maximum of the multiphoton absorption at energy densities up to 0.5 J/cm^2 is shifted very insignificantly to the "red" side.[13] The dashed curves in the same figure shows the absorption spectrum of the $^{13}CF_3I$ molecules.

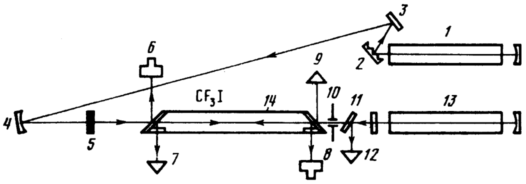

FIG. 1. Diagram of experimental setup: 1—TEA CO_2 laser, 2—diffraction grating, 100 lines/mm, 3,4—mirrors, 5—attenuator, 6,8—thermopile, 7,9, 12—photocell, 10—diaphragm, 11—plane-parallel plate, 13—excimer laser with photopreionization, 14—cell with CF_3I.

Figure 3a shows the dependence of the ultraviolet absorption cross section on the long-wave edge of the band at various densities of the infrared field, and also the cross section for the absorption of the unexcited molecules. The measurements were made at three frequencies corresponding to the generation frequencies of the ultraviolet lasers. The power density of the probing radiation is much less than the saturating density and amounts to ~10^{-6} J/cm^2. The measured values of the absorption cross section at $\lambda_{XeCl} = 308$ nm agreed with the values measured with the spectrophotometer. Fig. 3b shows the dependence of the cross section of ultraviolet absorption on the energy density at the entry to the cell (with allowance for the transmission of the window). The energy density ranged from 0.1 to 0.6 J/cm^2. It is seen from Fig. 3b that the cross section increases rapidly at low densities, after which the growth slows down. A particularly strong increase in the absorption is observed at the wavelength of the XeF laser. The solid lines in Fig. 4 show the increase of the absorption cross section of the excited molecules, relative to the absorption cross section of the unexcited molecules, as a function of the energy density for three wavelengths. The increase of the absorption at the wavelength of the XeF laser was ~200 at 0.6 J/cm^2.

The dependence of the ultraviolet absorption at the wave-length of the XeF laser on the delay time between

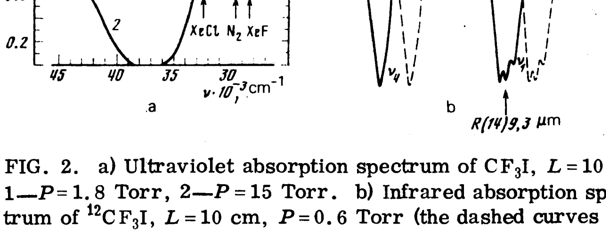

FIG. 2. a) Ultraviolet absorption spectrum of CF_3I, $L = 10$ cm: 1—$P = 1.8$ Torr, 2—$P = 15$ Torr. b) Infrared absorption spectrum of $^{12}CF_3I$, $L = 10$ cm, $P = 0.6$ Torr (the dashed curves show the absorption spectrum of $^{13}CF_3I$.

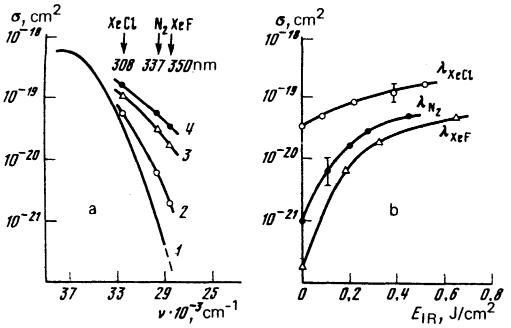

FIG. 3. a) Ultraviolet absorption spectrum of CF_3I molecules at various energy densities of the exciting infrared radiation: 1—$E=0.2-0.1$ J/cm², 3—0.3 J/cm² 4—0.5 J/cm². b) dependence of the ultraviolet absorption cross section on the energy density of the exciting infrared radiation for three wavelengths; P $(CF_3I)=0.25$ Torr.

the infrared and ultraviolet laser pulses is shown in Fig. 5. The energy density at the entry to the cell was 0.56 J/cm². With increasing delay, the absorption increases slightly, the reason being that the "tail" of the pulse contains 20% of the energy. If the ultraviolet pulse comes first, and then the infrared pulse, then the absorption does not change.

B. Calculation of ultraviolet absorption

The first electron absorption band in the ultraviolet region of the spectrum is due to the transition of the unbound p electron localized on the iodine atom by the "loosening" σ^* orbital, which covers mainly the carbon and iodine atoms.

An analysis of the ultraviolet absorption spectra of perfluoralkyl iodides shows that these spectra are determined by the presence of the C–I bond and are practically independent of the remainder of the molecule.[14] The maximum of the absorption spectrum occurs at 270 nm. As a result of light absorption in this band, the molecule dissociates, with unity yield, into the radical CF_3 and atomic iodine with excitation of the state $I(^2P_{1/2})$.

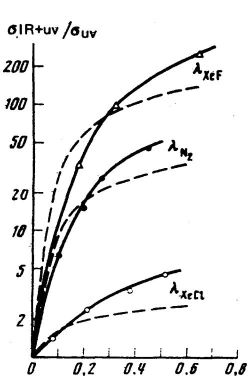

FIG. 4. Dependence of the ratio of the cross section of the ultraviolet absorption of excited molecules to the cross section of absorption of unexcited molecules on the infrared energy density for three wavelengths. The dashed curves show the calculation results.

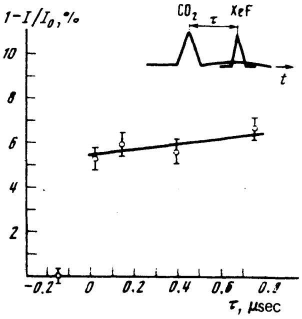

FIG. 5. Dependence of the absorbed energy on the delay time between the exciting infrared and the probing ultraviolet pulses.

A direct experimental determination of the yield of the excited $I(^2P_{1/2})$ and unexcited $I(^2P_{3/2})$ iodine atoms yields a value $\varphi=[I(^2P_{1/2})]/[I(^2P_{3/2})]=10.0$, i.e., 91% of the iodine atoms are in an excited state after the dissociation,[15] in good agreement with the theoretical analysis of the possible dissociation modes.[16]

The absorption cross section σ, i.e., the absorption coefficient per molecule, is determined by the overlap of the vibrational wave functions of the ground (ψ_v'') and excited (ψ_v') electronic states of the molecule[17]:

$$\sigma=A\nu\left[\int\psi_v''\psi_v'\right]^2, \qquad (1)$$

where ν is the transition frequency and A is the constant. In the calculation of the ultraviolet absorption, the CF_3I molecule can be regarded as quasidiatomic, and the main contribution to the absorption can be assumed to be made by the valence vibration $\nu_3=284$ cm⁻¹, see Fig. 6a. As will be shown below, in the considered frequency band (38,000–27,000 cm⁻¹) the absorption is determined by the population of the first ten vibrational levels. This corresponds to an excitation energy ~0.14 of the dissociation energy $D=18\ 780$ cm⁻¹.[18] It can be assumed that for such excitation levels the section of the potential surface and the CF_3–I coordinates is a parabola and the wave functions of the ground state are wave functions of

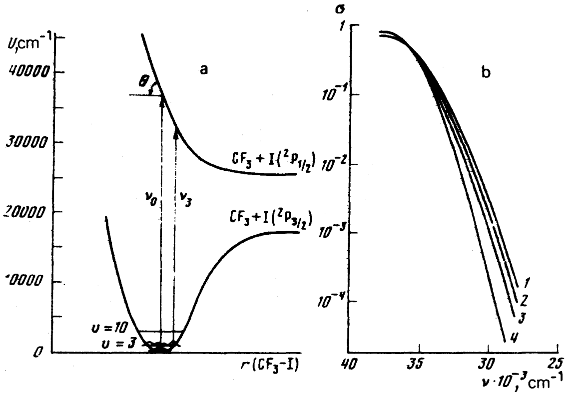

FIG. 6. a) Section of the potential surface of the CF_3I molecule in the coordinates CF_3-I ($\theta=42\ 000$ cm⁻¹/Å). b) Calculated dependence of the ultraviolet absorption cross section of the CF_3I molecules on the frequency: 1—$T=300$K, $\theta=44\ 000$ cm⁻¹/Å; 2—$T=300$ K, $\theta=42\ 000$ cm⁻¹/Å; 3—$T=300$ K, $\theta=40\ 000$ cm⁻¹/Å; 4—$T=200$ K, $\theta=42\ 000$ cm⁻¹/Å.

the harmonic oscillator:

$$\psi_k''=N_k\exp[-\xi^2/2]H_k(\xi), \tag{2}$$

where $N_k=(\alpha^{1/2}/\pi^{1/2}2^k k!)$ is the normalization factor; $H_k(\xi)=(-1)^k e^{-\xi^2}d^k(e^{-\xi^2})/d\xi^k$ are Chebyshev-Hermite polynomials, $\xi=\sqrt{\alpha}r$, $\alpha=m\omega_3/\hbar$. m is the reduced mass, and k is the number of the vibrational level.

Assuming that after dissociation all the iodine atoms are produced in an excited state, the potential function of the upper state can be approximated by one straight line with inclination angle θ near the equilibrium position r_e. The vibrational functions of this state are Bessel functions of order ±1/3, but replacement of these functions by δ functions at the classical turning points causes a negligible deviation from the exact calculations.[19]

The connection between the transition frequency ν, the number k of the vibrational level, and the distance r is determined by the relation

$$r=(\nu_m-k\nu_3-\nu)/\theta, \tag{3}$$

where $\nu_m=37,500$ cm^{-1} is the frequency corresponding to the maximum of the absorption spectrum. Thus, the cross section of the transition from the k-th level of the ground electronic state is given by

$$\sigma_k=B\nu N_k^2 e^{-\xi^2}H_k^2(\xi). \tag{4}$$

Absorption at a fixed frequency is the sum of absorptions from different vibrational levels:

$$\sigma=\sum_k n_k\sigma_k; \tag{5}$$

here

$$n_k=g_3\exp(-kh\nu_3/k_BT)\Big/\sum_k\exp(-kh\nu_3/k_BT)$$

is the Boltzmann population of the k-th level, T is the temperature of the gas, and g_3 is the degeneracy factor of the ν_3 mode.

The absorption spectrum was calculated with a computer. Variation of the inclination angle θ of the pontential curve made it possible to align the calculated spectrum with the measured one. Figure 6b shows the dependence of the absorption cross section on the frequency (curves 1–3) at different values of θ and at a temperature 300 K. Full agreement with the experiment is observed at $\theta=42\,000$ cm^{-1}/Å. The same figure (curve 4) shows the calculated absorption spectrum at $T=200$ K and at the obtained value of θ.

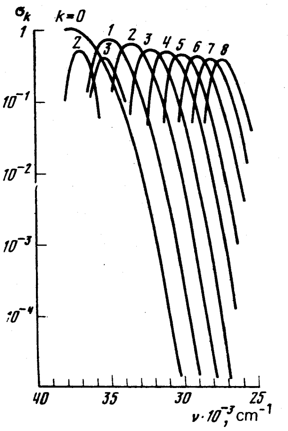

FIG. 7. Calculated frequency dependence of the absorption cross section for the CF$_3$I molecules from different vibrational levels of the electronic ground state.

Figure 7 shows calculated plots of the cross sections for absorption from different vibrational levels of the ground state of the CF$_3$I molecules against the frequency. It is seen that the main contribution to the absorption at a fixed frequency is made by a group of levels (~3–4 levels). The absorption on the edge of the band, at the XeF laser frequency, is due to the Boltzmann population of the vibrational levels $k=4$, 5, and 6. If all the molecules were at the zeroth vibrational level, then the absorption at 30 000 cm^{-1} would be 10^{-3} of the absorption at the maximum of the band.

C. Calculation of ultraviolet absorption under infrared excitation. Comparison with experiment.

The good agreement of the calculated ultraviolet absorption spectrum with the measured one at room temperature leads to the conclusion that the model is suitable for the description of the absorption by the CF$_3$I molecule. We consider on the basis of this model the ultraviolet absorption of CF$_3$I molecules whose vibrational levels are excited. The CO$_2$ laser emission is at resonance with the ν_1 mode, and the main contribution to the ultraviolet absorption is made by excitation of the ν_3 mode. This means that the laser energy absorbed in the ν_1 vibration becomes redistributed over the other vibrations.

At moderate energy densities not all the molecules interact with the infrared field but only a certain fraction q. What is determined in experimental investigations of multiquantum infrared absorption of molecules is the absorbed energy ε per molecule in the irradiated volume. Consequently, the molecule fraction q has a vibrational energy equal to ε/q. If the distribution of the molecule over the vibrational levels $n(k)$ were known, then we could calculate the dependence of the absorption cross section on the frequency by substituting this distribution in (5).

The ultraviolet absorption of vibrationally excited molecules was calculated by starting with the following simplified model. The distribution of the population in the ν_3 mode was assumed to be exponential with a temperature T_{eff}, i.e., during the time between the exciting and probing pulses the excitation is completely distributed over all the vibrational states of the excited molecule fraction q. The effective temperature was determined from the equation

$$\frac{\varepsilon}{q}+\sum_{i=1}^{6}\frac{g_ih\nu_i}{2}\operatorname{cth}\frac{h\nu_i}{2k_BT}=\sum_{i=1}^{6}\frac{g_ih\nu_i}{2}\operatorname{cth}\frac{h\nu_i}{2k_BT_{\text{eff}}}. \tag{6}$$

The second term in the left-hand side of the equation is the vibrational energy of the molecule at room temperature. The frequencies ν_i and the CF$_3$I molecule degeneracy factors g_i were taken from Ref. 20. It was also assumed that the $1-q$ molecules that do not interact with the infrared field are at room temperature. The total absorption is the sum of the absorption of the q mole-

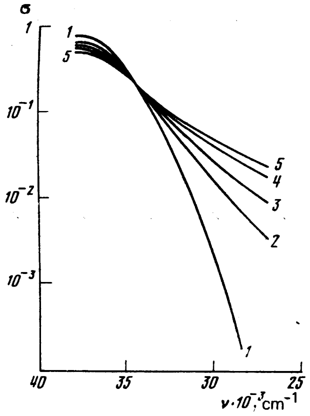

FIG. 8. Calculated dependence of the ultraviolet absorption cross section of CF_3I molecules on the frequency for different infrared energy densities: 1—$E_{IR} = 0$, 2—0.1 J/mc², 3—0.2, 4—0.4, 5—0.6.

cules with temperature T_{eff} and of the $1-q$ molecules with room temperature. The time of the collisional $V-V$ exchange and the time of the $V-T$ relaxation are much longer than the delay time between the infrared and ultraviolet pulses.

Figure 8 shows the calculated absorption spectrum at various infrared energy densities. The value of q was determined independently from the quantum yield of multiphoton dissociations of CF_3I and from the increase of the ultraviolet absorption when a buffer was added. The dashed curves of Fig. 4 are the results of the calculation of the relative increase of the absorption cross section as a function of the infrared energy density. It is seen that the agreement with the experimental data is satisfactory.

With increasing energy density, the experimental points lie higher than the calculated ones. This difference can be attributed to the following causes. First, it is assumed in the calculations that the distribution over the levels is exponential. It is shown in Refs. 13, and 21 that in the case of laser excitation the distribution has a steeper decrease on the high-energy side than the thermal distribution. Allowance for this fact should lead to better agreement. Second, we have assumed the CF_3I molecule to be quasidiatomic, neglecting the contribution made to the absorption by other modes; at high excitation levels this may be incorrect. It was also assumed in the calculation that θ does not depend on the distance between the nuclei. It is qualitatively clear that when this dependence is taken into account the absorption should be larger on the long-wave edge, since the contribution at this frequency comes from a larger number of vibrational levels.

4. SEPARATION OF CARBON ISOTOPES

As shown in the preceding chapter, the multiphoton vibrational excitation of the molecules leads to a sharp increase of the ultraviolet absorption on the edge of the electronic absorption band. This effect can be used to separate isotopes. It is known that the difference between the ultraviolet absorption cross sections of molecules containing atoms of different isotopes is negligible.[22] Therefore ultraviolet irradiation of CF_3I causes the molecules containing ^{12}C and ^{13}C to dissociate in degrees. In fact, when CF_3I is irradiated only with an XeCl laser, no enrichment in the dissociation products is observed.

Under vibrational excitation of molecules in the absorption band of one isotope, a predominant increase in the absorption of the molecules containing this isotope takes place. The selectivity S_2 of the monomolecular process of dissociation is determined by the relative increase of the absorption cross section of the vibrationally excited molecules: $S_2 = \sigma_{IR+UV}/\sigma_{UV}$. At sufficiently high infrared radiation density, multiphoton ionization also takes place and its selectivity S_1 is determined by the overlap of the multiphoton absorption spectra. The total selectivity is a combination of the selectivity along the IR and IR + UV dissociation channels:

$$S = \frac{\beta_1 S_1 + (1-\beta_1)\beta_2 S_2}{\beta_1 + (1-\beta_1)\beta_2}, \tag{7}$$

where β_1 and β_2 are the dissociation yields, i.e., the fractions of the molecules dissociated per pulse in the irradiated volume.

The experimental conditions can be chosen such that the time of the vibrational $V-V$ exchange is much longer than the delay time between the exciting infrared pulse and the dissociating ultraviolet pulse, and the dissociation yield under the influence of the infrared pulse only is much less less than the dissociation yield under IR + UV excitation.

In the experiment, the $^{12}CF_3I$ molecules were vibrationally excited on the $R(14)$ line of the 9.3 μm band of the CO_2 laser. The infrared absorption spectrum of the $^{13}CF_3I$ molecules is shifted towards lower frequencies by 26 cm⁻¹–Fig. 2b. At an infrared pulse energy density 0.24 J/cm², the dissociation yield β_1 of the infrared radiation is 10^{-4} (Ref. 13), and the dissociation yield in IR + UV excitation is $\beta_2 = 10^{-3}$ for $\lambda_{XeF} = 351$ nm. For the shorter wavelength $\lambda_{XeCl} = 308$ nm we have $\beta_2 = 10^{-2}$. Thus, the dissociation of the CF_3I molecules follows the scheme

$$^{12}CF_3I + nh\nu_{IR} \rightarrow {}^{12}CF_3I^*,$$
$$^{12}CF_3I + h\nu_{UV} \rightarrow {}^{12}CF_3 + I(^2P_{1/2}).$$

The end products of the photolysis are C_2F_6 and I_2:

$$CF_3 + CF_3 \rightarrow C_2F_6, \quad I + I \rightarrow I_2.$$

Thus, when $^{12}CF_3I$ molecules are vibrationally excited they are predominantly dissociated by the ultraviolet radiation and the products are enriched with the ^{12}C isotope. The points in Fig. 9 show the selectivity of the process of the sequential IR–UV dissociation of CF_3I, which coincides, when a small amount of matter is produced, with the enrichment coefficients in the products

$$\alpha = [^{12}C/^{13}C]_i / [^{12}C/^{13}C]_f,$$

as a function of the measured ratio of the absorption cross section at an infrared energy density 0.24 J/cm² and for unexcited molecules $\sigma_{IR+UV}/\sigma_{UV}$. The measurements were made with XeF and XeCl laser radiation. The straight line corresponds to the ideal case when the

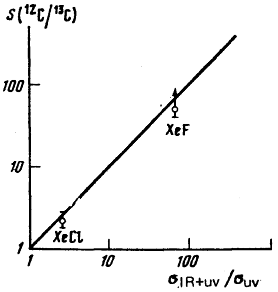

FIG. 9. Dependence of the selectivity in the dissociation products (C_2F_6) on the relative increase of the absorption cross section for λ_{XeCl}, λ_{XeF}; $E_{IR} = 0.24$ J/cm^2.

selectivity of the excitation and of the subsequent dissociation is equal to the relative increase of the absorption cross sections. The experimentally determined values of S are 2.3 for λ_{XeCl} and ≥ 48 for λ_{XeF}, in satisfactory agreement with the measured increase of the absorption (Fig. 4).

An effective method of increasing the selectivity may be lowering the temperature of the irradiated gas. Figure 5b shows the calculated absorption spectrum of CF_3I at $T = 200°\,K$ (curve 4). This temperature the absorption at the lasing wavelength of the XeF laser decreases by a factor of 10, but under vibrational excitation the absorption cross section should not decrease. In addition, when the temperature is lowered its absorption of molecules of the other isotopes at resonance with the CO_2 laser emission decreases.

The selectivity can be decreased by the secondary chemical exchange reactions

$$^{12}CF_3+^{13}CF_3I \rightarrow ^{12}CF_3I+^{13}CF_3.$$

To decrease the probability of secondary chemical reactions it is necessary to bind rapidly the photodissociation products. A good acceptor of the CF_3 radicals is oxygen, which forms, in particular, COF_2 when interacting with CF_3. Addition of oxygen increases also of the fraction of the molecules that interact with the infrared field. The ultraviolet absorption is then increased, and the dissociation yield under only infrared excitation decreases. Figure 10 shows the dependence of the yield of the dissociation of the CF_3I molecules mixed with oxygen (1:100) at a total pressure 20 Torr on the CO_2 laser energy density ($\lambda_{UV} = 308$ nm). The relative dissociation yield w was determined from the formula $n = n_0 e^{-(wN)}$, where N is the number of pulses, $w = \sigma E/s$, σ is the absorption cross section, E is the ultraviolet laser energy (in photons per pulse), s is the area of the ultraviolet radiation in the cell, and n_0 and n are the numbers of the CF_3I molecules before and after the irradiation. The 1928 cm^{-1} band of COF_2 appears in the infrared absorption spectrum after the irradiation.[23] The more intense 1249 cm^{-1} band coincides with the absorption band of C_2F_6. For comparison, the dashed curve in Fig. 10 shows an interpolation of the data of Ref. 13 on the yield of the dissociation of CF_3I molecules irradiated only by a CO_2 laser. The infrared energy density must be chosen such that $\beta_2 \gg \beta_1$. This can always be done, since the yield of multiphoton dissociation has a very strong power-law dependence on the infrared energy density, for example, $\beta_1 \sim E_{IR}{}^5$ for CF_3I.

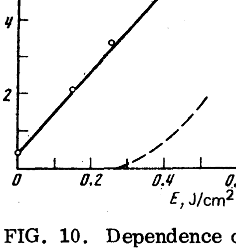

FIG. 10. Dependence of the dissociation yield of the CF_3I molecules on the energy density of the exciting infrared radiation in sequential IR–UV excitation. Mixture $CF_3I{:}O_2 = 1{:}100$, $P(CF_3I) = 0.2$ Torr. The dashed curve shows the dependence of the dissociation yields in radiation from only a CO_2 laser.[13]

5. CONCLUSION

In the present paper we have shown, with the CF_3I molecule as an example, that the ultraviolet absorption of a vibrationally excited molecule can be satisfactorily explained by using the model of total redistribution of the absorbed energy among all the vibrational states with an approximately exponential distribution of the populations. The fact that a clearly defined vibration appears in the ultraviolet absorption makes it possible to organize an experiment aimed at determining the time of the intermode energy transfer. This question is presently very important for the understanding of the process of collisionless dissociation of molecules in the field of an infrared laser.

The method of successive IR–UV excitation is promising from the point of view of selective action on molecules. It can be used for isotopes separation. Particular interest attaches to the use of this method for molecules for whose absorption region there are no powerful infrared lasers, since successive IR–UV excitation makes it possible to increase the infrared energy density. This method seems promising for separation of isotopes of heavy elements. The point is that when the atomic number of the element is increased, the isotopic shift in the absorption spectra decreases. Therefore the use of a strong infrared field for collisionless dissociation of the molecules containing these elements leads to a small selectivity of the process. In this case moderate infrared intensities must be used only for preliminary excitation, and the dissociation is effected with an ultraviolet laser. To increase the absorption in the ultraviolet stage, the infrared excitation can be produced by two lasers, one of low power in the resonant absorption band and an intense one for the excitation of an appreciable fraction of the molecules.

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Modulation excitation of magnetic fields

S. A. Bel'kov and V. N. Tsytovich

P. N. Lebedev Physics Institute, USSR Academy of Sciences

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A new collisionless mechanism is proposed for spontaneous excitation of magnetic fields in a medium with intense electrostatic oscillations. It is shown that the strong electrostatic oscillations are unstable to excitation of magnetic fields. Nonlinear self-consistent equations are obtained for the excitation of the magnetic fields. These equations take into account the influence of the generation of magnetic fields by the electrostatic oscillations. It is shown that in a plasma at $E^2/4\pi nT \ll (c^4 v_{Te}{}^4) m_e/m_i$ the growth rate of the modulation excitation of the magnetic fields coincides approximately with the growth rate of the modulation excitation of the inhomogeneities of the concentration. The excitation of both magnetic fields and density inhomogeneities is investigated for the case when the inverse inequality holds.

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1. INTRODUCTION

The excitation of magnetic fields is of interest both in astrophysical applications (the nature of the galactic magnetic fields, of sunspots, and others) and when it comes to explain the observed excitation of strong magnetic fields in a plasma that absorbs intense electromagnetic radiation (up to 10^3 G in Refs. 1 and up to 10^6 G according to the estimates of Refs. 2 and 3). A number of models were proposed to explain this phenomenon (see Refs. 4–11). These models are based either on the concept of inductive generation of magnetic fields by the thermal emf produced in the expanding plasma,[2,4,7] or on the concept of resonant absorption of radiation near the plasma frequency.[5,6,8-10] A more accurate analysis[7] has shown that in models with a thermal emf there is no actual generation of the magnetic fields, only their convective enhancement. It is important that in all the foregoing models collisions play a rather important role, and there should be no excitation in the absence of collisions (in the collisionless regime). Recent experiments[10,12] in the radio-frequency field have shown, however, that the excitation of magnetic fields takes place also in the absence of collisions.

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