

SELECTIVE DISSOCIATION OF C₄F₉ COI MOLECULES BY THE SECOND-HARMONIC RADIATION OF PULSED TEA CO₂ LASER

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IR multiphoton dissociation of C₄F₉ COI was studied by the second-harmonic radiation of TEA CO₂ laser. The stretching vibration of the carbonyl bond $\nu_{C=O}$ was excited. The second harmonic of CO₂ laser was generated with the use of nonlinear crystal AgGaSe₂. The maximum energy fluence at focus was $\Phi \approx 1.2 \text{ J/cm}^2$. The MPD of C₄F₉ COI was proved to be effective and selective with respect to oxygen and carbon isotopes. The main dissociation products were C₄F₉I and CO. The dissociation product, CO, was enriched with both ¹⁶O and ¹²C when the C₄F₉ COI molecule was excited at the center of the band $\nu_{C=O}$ by the laser line 10P(18) with $2\omega_{\text{las}} = 1797.2 \text{ cm}^{-1}$. The maximum selectivities measured for oxygen and carbon were $\alpha(16/18) = 20$ and $\alpha(12/13) = 25$ respectively.

KEY WORDS: CO₂ laser, second harmonic, carbonyl compound, multiphoton dissociation, isotopic selectivity.

INTRODUCTION

Compounds containing a carbonyl group ($>C=O$) are considered to be rather promising for selective IR multiphoton dissociation (MPD) which can be used in laser synthesis of compounds as well as in isotope separation.¹ The stretching vibration of the bond $-C=O$ ($\nu_{C=O}$) in carbonyl-containing compounds occurs in the IR absorption spectra as an intense and characteristic band in the range $\sim 1700\text{--}1800 \text{ cm}^{-1}$ (see Reference 2) and has large isotope shifts (30 to 50 cm^{-1}) for carbon and oxygen³ which is important for obtaining a high isotopic selectivity of MPD. The frequency $\nu_{C=O}$ falls within the operation region of CO laser. The isotopically selective MPD under pulsed CO laser radiation was first reported in Reference 4. As a result of IR MPD of COCl₂ molecules the residual gas (COCl₂) was enriched with C¹² and O¹⁶.

At the same time, the CO laser has a number of shortcomings, such as a long pulse ($\sim 5 \mu\text{s}$) and a rare generation spectrum. The double-frequency radiation of the TEA CO₂ laser, the most economical and efficient laser source in the IR range, could be more convenient in exciting carbonyl compounds.

In the present work we studied the MPD of C₄F₉COI molecules (perfluorovaleryl iodide) by the second-harmonic radiation of a pulsed TEA CO₂ laser. Nonlinear AgGaSe₂ monocrystals (silver selenogallate) were used for effective generation of the second harmonic.

EXPERIMENT

C_4F_9COI was synthesized, with its purity of 98 to 99%, by L. E. Deev *et al.* from Perm branch of the State Institute of Applied Chemistry. Before the experiment the substance was purified by trap to trap low-temperature vacuum distillation. The saturation pressure vapor of the compound was 29 Torr at $t = 21 \pm 2^\circ C$. Butyl iodide (C_4F_9I) synthesized at the same laboratory was used to identify the dissociation products.

The C_4F_9COI molecules were dissociated using the second-harmonic radiation of a tunable TEA CO_2 laser that operated on the mixture $^{13}CO_2:N_2:He = 1:0.15:4$. The irradiation pulse was standard in shape, it had a peak with its halfwidth of about 80 ns and "a tail" with a total duration of about 1 μs . The peak contained more than 70% of pulse energy. The $AgGaSe_2$ crystal was used as a nonlinear element to generate the second-harmonic of CO_2 laser. The CO_2 laser radiation was collimated with a system of mirrors and NaCl lenses and directed to the $AgGaSe_2$ crystal. At the output of the crystal the radiation with the $2\omega_{las}$ frequency was separated from the CO_2 laser radiation (ω_{las}) with a LiF plate, focused by a NaCl lens with the focal length $f = 13$ cm and directed into a stainless-steel cell 11.2 cm long, with its internal diameter of 1.2 cm and NaCl windows.

The second-harmonic radiation of CO_2 laser excited C_4F_9COI within the range $2\omega_{las} = 1779.6 \div 1810.8$ cm^{-1} which corresponded to the $^{13}CO_2$ generation lines 10P(10) \div 10P(28). In some experiments the C_4F_9COI molecules were excited by the radiation of the CO_2 laser itself. In this case both a quasi-parallel beam with its fluence $\Phi \simeq 3.0$ J/cm^2 and a focused beam (a lens with $f = 40$ cm) with its fluence in the waist $\Phi = 5.7 \div 10$ J/cm^2 were used.

The irradiation procedure and product analysis were analogous to those described in Reference 5. The review IR spectra of C_4F_9COI and dissociation products were recorded by a SPECORD-75IR spectrophotometer. The consumption of parent C_4F_9COI was determined from the IR spectra measured before and after irradiation. Then the parameter $\beta\Gamma$, the fraction of molecules dissociated in a pulse, was calculated (the notations and the transformed formula are taken from Reference 6).

$$\beta\Gamma = 1 - \left[\frac{\ln(I_2/I_1)}{\ln(I_1/I_0)} \right]^{1/N},$$

where N is the number of irradiation pulses; I_1 and I_2 are the peak intensities of the band $\nu_{C=O}$ before and after irradiation, Γ is the ratio of the exposed gas volume to the total volume of the cell.

We did not calculate the dissociation yield β for focused irradiation but just estimated it approximately because the fluence Φ at the $2\omega_{las}$ frequency varied by several times along the whole cell. In the case of irradiation at the ω_{las} frequency we used a quasi-parallel beam, so the dissociation yield β was calculated accurately.

A mass spectrometer was used to study the selectivity of C_4F_9COI MPD from the variation of isotopic ratios in the dissociation product CO in the mass peaks with $m/e = 28, 29, 30$ corresponding to the molecular ions $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$. The ^{16}O - and ^{12}C -enrichment factors in the CO product (K_{pr}) in our conditions

when the consumption of parent gas did not exceed 10% were equal to the MPD selectivity⁶ and defined as

$$\alpha(16/18) \simeq K_{\text{pr}}(16/18) = \frac{[^{16}\text{C}]_{\text{pr}} \cdot [^{16}\text{C}]_0}{[^{18}\text{C}]_{\text{pr}} \cdot [^{18}\text{C}]_0},$$

$$\alpha(12/13) \simeq K_{\text{pr}}(12/13) = \frac{[^{12}\text{C}]_{\text{pr}} \cdot [^{12}\text{C}]_0}{[^{13}\text{C}]_{\text{pr}} \cdot [^{13}\text{C}]_0}$$

where $^{16}\text{C}_{\text{pr}}$, $^{18}\text{C}_{\text{pr}}$, $^{12}\text{C}_{\text{pr}}$, $^{13}\text{C}_{\text{pr}}$ are the concentrations of the isotopes in CO; $^{16}\text{C}_0$, $^{18}\text{C}_0$, $^{12}\text{C}_0$, $^{13}\text{C}_0$ are the natural concentrations of the isotopes in the gas before irradiation.

RESULTS AND DISCUSSION

Figure 1 presents the IR spectrum of C₄F₉COI in the spectral region 2000–600 cm⁻¹. The most intensive bands are 1796, 1362, 1330, 1254, 1231, 1167, 1148, 958, 900, 812, 783, 749, 734 cm⁻¹. As far as we know, the IR spectrum of this compound and the assignment of the vibrations are absent in literature. The band with the 1796 cm⁻¹

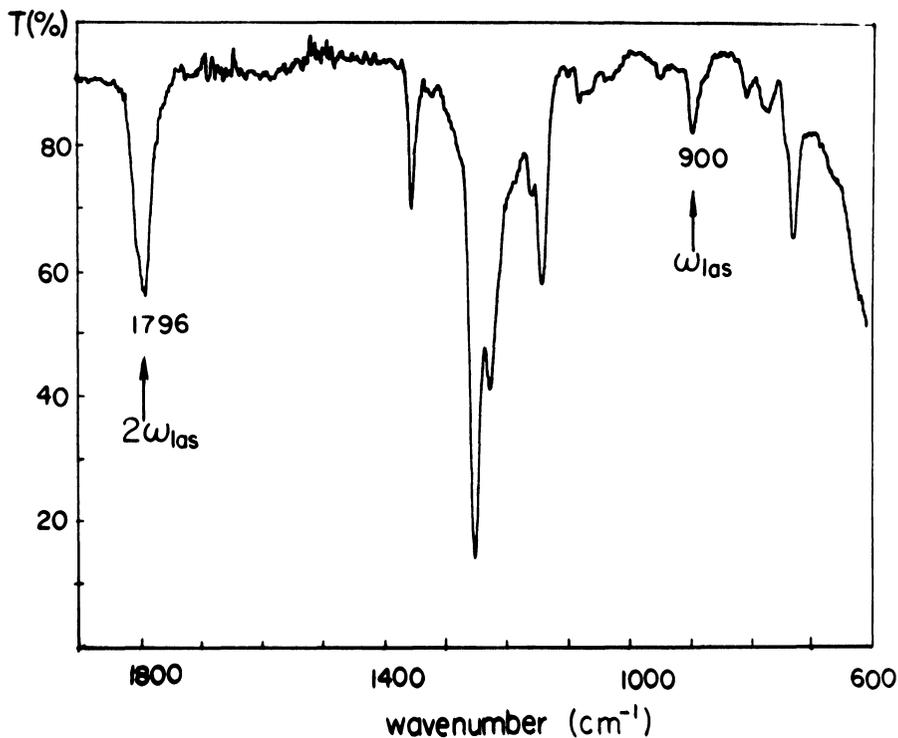


Figure 1 IR spectrum of C₄F₉ COI vapor. Gas pressure is 1 Torr. Cell length is 11.2 cm.

frequency is unambiguously assigned to $\nu_{C=O}$.² The absorption factor at the peak of this band is $k = 24 \pm 2 \text{ atm}^{-1} \text{ cm}^{-1}$.

There is a comparatively weak band in the 900 cm^{-1} region. The assignment of fluorocarbons bands in this region^{7,8} may suggest that this band (900 cm^{-1}) contains a certain percentage of C_5 stretching skeletal vibration. We denoted it as ν_{C-C} for short. Thus, C_4F_9COI molecules can be excited in two ways through the vibration $\nu_{C=O}$ by radiation with $2\omega_{\text{las}}$ and through ν_{C-C} by radiation with ω_{las} .

Figure 2 presents the parameter $\beta\Gamma$ as a function of the radiation frequency $2\omega_{\text{las}}$ at the $\nu_{C=O}$ excitation. The MPD spectrum was measured with the radiation fluence at focus $\Phi \approx 0.5 \text{ J/cm}^2$. This figure also shows a linear absorption spectrum for the $\nu_{C=O}$ band. It can be seen that in its position and halfwidth the MPD spectrum practically coincides with the linear absorption spectrum for the band $\nu_{C=O}$. The absence of a characteristic "red" shift of IR MPD spectrum was observed before in the case of MPD of such polyatomic molecules as $[UO_2(\text{hfacac})_2]_2$.⁹

The dependence of the $\beta\Gamma$ parameter on the incident radiation energy E was obtained for the frequency $2\omega_{\text{las}} = 1797.2 \text{ cm}^{-1}$ coinciding with the center of the linear absorption band $\nu_{C=O}$ (Figure 3). This dependence is nearly quadratic. It

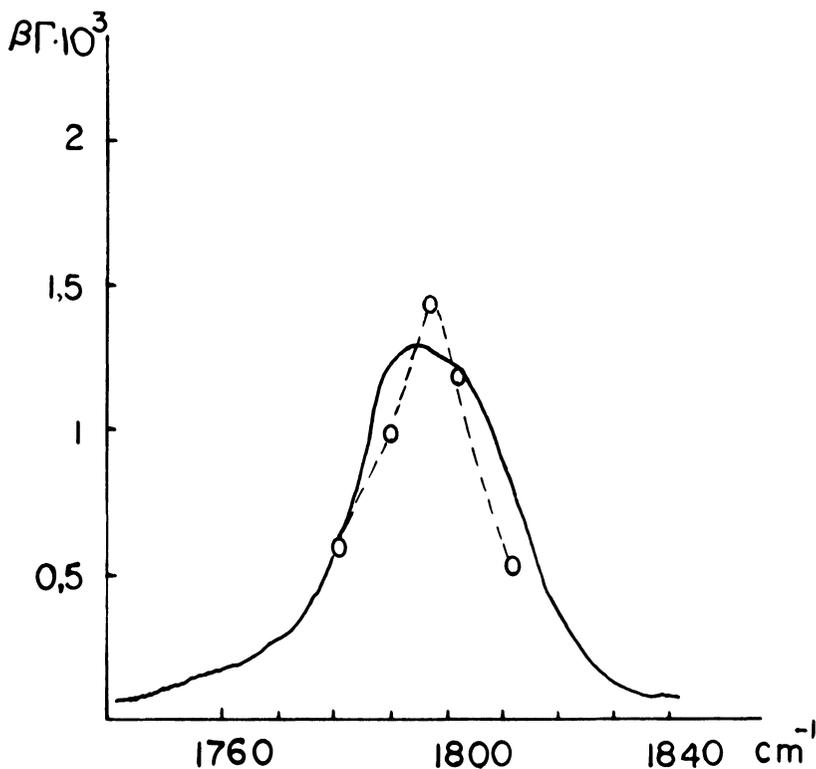


Figure 2 Dependence of $\beta\Gamma(0)$ on the exciting laser radiation frequency $2\omega_{\text{las}}$ and the linear absorption spectrum of the band $\nu_{C=O}$ (solid line). Pressure is 1 Torr. $\Phi_{\text{waist}} = 0.5 \text{ J/cm}^2$.

should be noted that the efficiency of C_4F_9COI MPD by second-harmonic radiation of CO_2 laser is rather high. Our estimations show that the dissociation yield can reach $\sim 100\%$ when the second harmonic fluence at focus $\Phi \approx 1.2 \text{ J/cm}^2$.

The isotopic selectivity was measured as the "rich" isotope $C_4F_9C^{16}OI$ was excited at the center of the band $\nu_{C=O}$ at the frequency $2\omega_{las} = 1797.2 \text{ cm}^{-1}$. The dissociation product CO was enriched both with ^{16}O and ^{12}C . Figure 4 shows the dependence of the selectivities $\alpha(16/18)$ and $\alpha(12/13)$ on the C_4F_9COI pressure. The exponential decrease of the dissociation selectivity α observed with an increase in the parent gas pressure ($P = 0.2 \div 1 \text{ Torr}$) is typical of MP excitation of the "rich" isotope.⁶ The maximum values of selectivity $\alpha(16/18) = 20$ and $\alpha(12/13) = 25$ were obtained with $P = 0.2 \text{ Torr}$. Besides mass spectrometry of CO , other dissociation products were analyzed using their IR spectra. After irradiation of $1 \text{ Torr } C_4F_9COI$ by second-harmonic radiation with $\Phi_{max} = 1, 2 \text{ J/cm}^2$ up to 50% consumption was observed only one product— C_4F_9I (new IR bands with $\nu = 685, 716, 1093 \text{ cm}^{-1}$). Identification was performed by comparing the product spectrum with the IR spectrum of pure C_4F_9I . The concentration of the product (C_4F_9I) increased proportionally with the consumption of the parent gas.

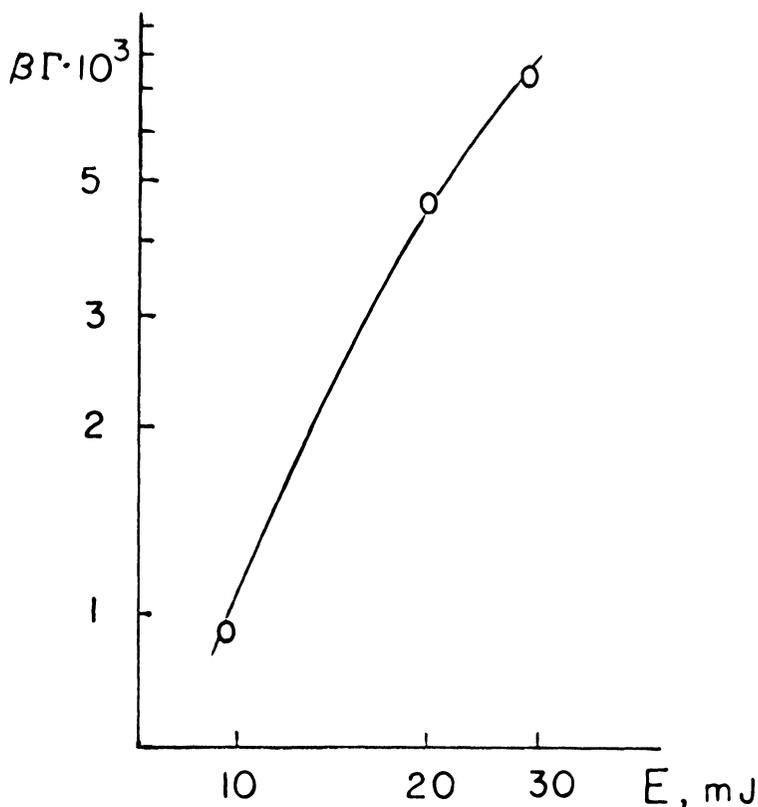


Figure 3 Dependence of $\beta\Gamma$ on incident laser radiation energy. $P_{C_4F_9COI} = 1 \text{ Torr}$, $2\omega_{las} = 1797.2 \text{ cm}^{-1}$.

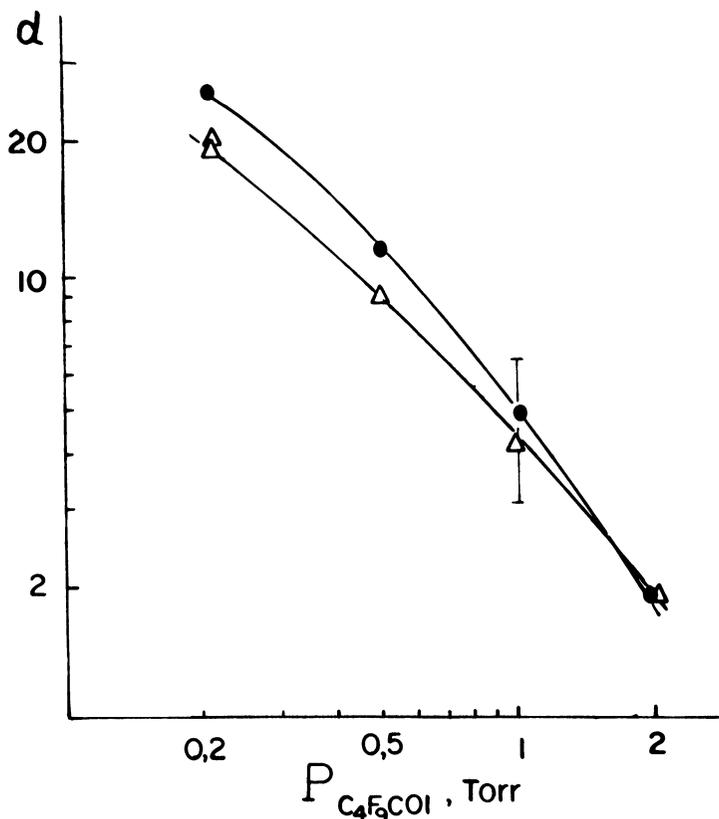
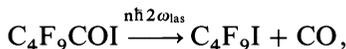


Figure 4 Dependence of selectivity α on parent gas pressure. $2\omega_{\text{las}} = 1797.2 \text{ cm}^{-1}$, $\alpha(16/18)$ — Δ ; $\alpha(12/13)$ — \bullet ; $\Phi_{\text{waist}} \approx 0.5 \text{ J/cm}^2$.

Since we observed only C_4F_9I and CO as final products, we can assume C_4F_9COI molecules dissociate as follows:



and, thus, all the oxygen atoms from dissociated C_4F_9COI transfer to CO . This agrees with the known data about the unimolecular dissociation of carbonyl-containing compounds.^{1,4}

Besides the dissociation of C_4F_9COI in the process of excitation of $\nu_{C=O}$, we dissociated these molecules using CO_2 laser radiation ($\omega_{\text{las}} = 898.6 \text{ cm}^{-1}$) when exciting a vibration with $\nu = 900 \text{ cm}^{-1}$, supposedly ν_{C-C} . In this case we calculated the dissociation yield of the main isotope component $C_4F_9C^{16}OI$ which, with $\Phi = 3 \text{ J/cm}^2$ (quasi-parallel geometry), was $\beta_{16} \approx 2\%$. Unlike the quadratic dependence on E when $\nu_{C=O}$ is excited, this dependence on Φ has a more sharp form, $\beta_{16} \approx \Phi^5$. The dissociation products differ too. If in the case of low Φ there are distinct C_4F_9I bands observed in the IR spectrum, with an increase in Φ bands

characteristic of C₂F₄ [1337 and 1186 cm⁻¹ (Reference 7)] and C₂F₅I [1113, 923 cm⁻¹ (Reference 8)] appear and become more intense. The amount of dissociated C₄F₉COI is balanced with that of resultant products. This allows us to assume that there are two channels of final product formation:



with channel (2) being realized at higher Φ . When the MPD yield of C₄F₉COI is about 100%, the yields of C₄F₉I and C₂F₄ are the same (within the experimental error $\pm 10\%$). This enables us to assume that the difference between the activation energies E₁ and E₂ of channels (1) and (2) is small as compared to the absolute values E₁ and E₂.

It should be noted that the initial step in the IR MPD of C₄F₉COI is probably the break of the weakest C–I bond in the both cases (2 ω_{las} , ω_{las} radiation).

What is the cause of formation of different final MPD products of C₄F₉COI when we excite the bands $\nu_{\text{C=O}}$ and $\nu_{\text{C-C}}$? There are some reasons for it. First, the observed difference in products can be explained by the fact that rather different vibrational energy distribution functions of molecules are formed under different conditions of excitation at ω_{las} and 2 ω_{las} . Although the dissociation yield in the case of excitation at ω_{las} is lower than the one at 2 ω_{las} (2% at $\Phi_{\omega, \text{min}} = 3 \text{ J/cm}^2$ as against $\sim 100\%$ at $\Phi_{2\omega, \text{max}} = 1.2 \text{ J/cm}^2$), the excited molecules in the first case may have a higher average vibrational energy. So, these molecules will probably decompose via a high-energy channel with E₂.

Second, the difference in MPD products may be caused by the subsequent dissociation of the primary product C₄F₉I to C₂F₄ and C₂F₅I at the ω_{las} frequency. This, however, is possible only for vibrationally excited C₄F₉I. A similar fact was observed at MPD of C₂F₆ sensitized by vibrationally excited CF₃I molecules.¹⁰ Under standard conditions the C₄F₉I molecule does not dissociate under the action of radiation with $\omega_{\text{las}} = 898.6 \text{ cm}^{-1}$ which was proved by us in some additional experiments. This is not surprising because the nearest IR band of C₄F₉I is shifted to the short-wave length region ($\sim 30 \text{ cm}^{-1}$) from ω_{las} .

Third, it is quite possible that the formation of various MPD products of C₄F₉COI excited through the modes $\nu_{\text{C=O}}$ and $\nu_{\text{C-C}}$ results from the nonstatistical decay of C₄F₉COI.

Besides, we dissociated the C₄F₉COBr and BrCF₂COBr molecules using the second-harmonic radiation of TEA CO₂ laser. The efficiency of the MPD of these molecules was rather high too.

CONCLUSION

The experiments performed have shown that compounds like C₄F₉COX (X = Br, I) and BrCF₂COBr can dissociate effectively when the modes of the carbonyl group are excited by the second-harmonic radiation of TEA CO₂ laser.

The C₄F₉COI molecule was used to show that when this molecule is excited by

the second harmonic of CO₂ laser, the primary MPD products are C₄F₉I and CO, whereas the products are C₄F₉I, C₂F₄, C₂F₅I and CO in the case of excitation by CO₂ laser pulses.

The MPD of C₄F₉COI is selective with respect to oxygen and carbon isotopes at the excitation of the C₄F₉COI molecules in the center of the band $\nu_{C=O} = 1786 \text{ cm}^{-1}$. The product of unimolecular dissociation of C₄F₉COI–CO is enriched with ¹⁶O and ¹²C. The selectivities measured from the variation of isotope ratio in CO were $\alpha(16/18) \simeq 20$ for oxygen and $\alpha(12/13) \simeq 25$ for carbon.

The obtained primary selectivities ($\alpha \geq 20$) are rather high and reflect the spectral properties of C₄F₉COI MPD. Thus, the assumption that carbonyl-containing compounds are promising for laser separation of oxygen isotopes when they are excited through the vibration $\nu_{C=O}^1$ is experimentally proved by the results of the present work.

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