

THE SPECTRAL FEATURES OF POLYATOMIC MOLECULES MULTIPHOTON EXCITATION IN A STRONG IR-LASER FIELD

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The experimental data on multiphoton excitation of polyatomic molecules in strong fields of high pressure continuously tunable CO₂ lasers are presented. The program package for computer simulation of multiphoton excitation spectra and excitation dynamics is developed. Good agreement between computer simulation and experimental data is observed.

INTRODUCTION

Since the first observation of multiphoton dissociation (MPD) of polyatomic molecules in a strong IR laser field¹ and demonstration of isotopic selectivity of MPD² the process of collisionless multiphoton excitation (MPE) of polyatomic molecules have been investigated in many laboratories (see reviews^{3–4}).

It was demonstrated that the main features of MPE are dominated by the complex structure of vibrational-rotational spectrum of polyatomic molecules. In particular, it was generally accepted to divide vibrational spectrum of polyatomic molecules into two qualitatively different regions: the region of low lying discrete levels (DL) and the region called quasicontinuum (QC) of vibrational states. Respectively MPE has qualitatively different features in these two regions. MPE in the DL region is the coherent excitation via one and multiphoton transitions. The efficiency of excitation in this region reveals the sharp resonance dependence on laser frequency that is determined by the spectral structure of rotation-vibration spectrum of DL. It is this stage of excitation that provides the isotopic selectivity of MPD. In contrast, the incoherent excitation in QC via ladder switching one photon transitions is the dominating process of MPE because the anharmonicity mode mixing leads to the high density of one photon dipole allowed transitions. The form factor of such one photon bands in QC is assumed to be a widely broadened. It explains the smooth dependence of the MPE efficiency in QC region on the excitation frequency. The ladder switching excitation in QC provides the high efficiency of MPD at moderate intensity of exciting radiation with fixed frequency. The qualitative difference of the excitation process in first and second stages makes it possible to search the optimal way of MPD by using of two or three laser frequency irradiation with each laser pulse frequency being optimal for an appropriate excitation stage. The multifrequency

excitation of polyatomic molecules gives reach opportunities to conserve the sharp resonance structure and to dissociate a molecule with high efficiency simultaneously. To realize these opportunities as the experimental investigation of spectral features of multifrequency excitation as soon as the theoretical analysis of excitation process based on the comprehensive set of molecular spectroscopic constants are necessary.

The subject of this work is the survey analysis of experimental data on MPE, MPD spectroscopy obtained in the last years in our group with the help of continuously tunable CO₂ lasers and the developing of computer simulation of MPE process in a strong IR laser field. An adequate description of MPE process needs a detailed information about vibrational-rotational spectra of excited vibrational states of polyatomic molecules. The additional information which is necessary to distinguish between the contributions of different multiphoton transitions into MPE and MPD spectra can be obtained with the use of nonlinear spectroscopy techniques. That is why the results presented in this paper were obtained by four experimental techniques: (1) spectral measurements of absorbed energy; (2) spectral measurements of dissociation yield; (3) four wave mixing spectroscopy; (4) third harmonic generation spectroscopy.

The second direction developed in this work is the computer simulation of MPD and MPE spectra. The advantage of computer simulation is concerned with the ability to calculate with the help of computer the MPD and MPE spectra in details without conducting routine and complicated experiments. Such calculations need a comprehensive set of molecular spectroscopic constants which can be obtained from the available linear spectra of one photon transitions between excited states and overtone spectra of a mode under investigation. The comparison between the calculated and observed IR multiphoton spectra of polyatomic molecules presented in this work justify that digital experiment is a reliable way to obtain information about MPE spectra of different molecules.

ABSORPTION SPECTROSCOPY

Energy absorbed in the gas was measured opto-acoustically. The gas cell was equipped with opto-acoustic detector. To eliminate the effect of hot bands the gas mixtures were cooled down to 140 K in a gas cell when investigating DL excitation spectra. The DL excitation spectra were studied by high-pressure continuously tuned CO₂ laser with e-beam sustained discharge. This laser was described in Reference 5. The laser pulse duration was 40 ns, its energy reached 1 J cm⁻². The spectral width of emission was less than 0.03 cm⁻¹, the total range of continuous tuning was 86 cm⁻¹, the increment of tuning was 0.03 cm⁻¹ in contrast with the line tuned TEA CO₂ laser increment 1.7 cm⁻¹. The frequency of laser pulse was controlled with Fabri-Perot interferometer and opto-acoustic detector with reference gases N₂O and CO₂.

Figure 1 displays the absorption spectra of SF₆ molecules at resonant excitation of triply degenerated v_3 mode that were published in Reference 6. The energy fluence of CO₂ laser pulse was 0.09 J cm⁻² and 0.27 J cm⁻². The total pressure of gas mixture

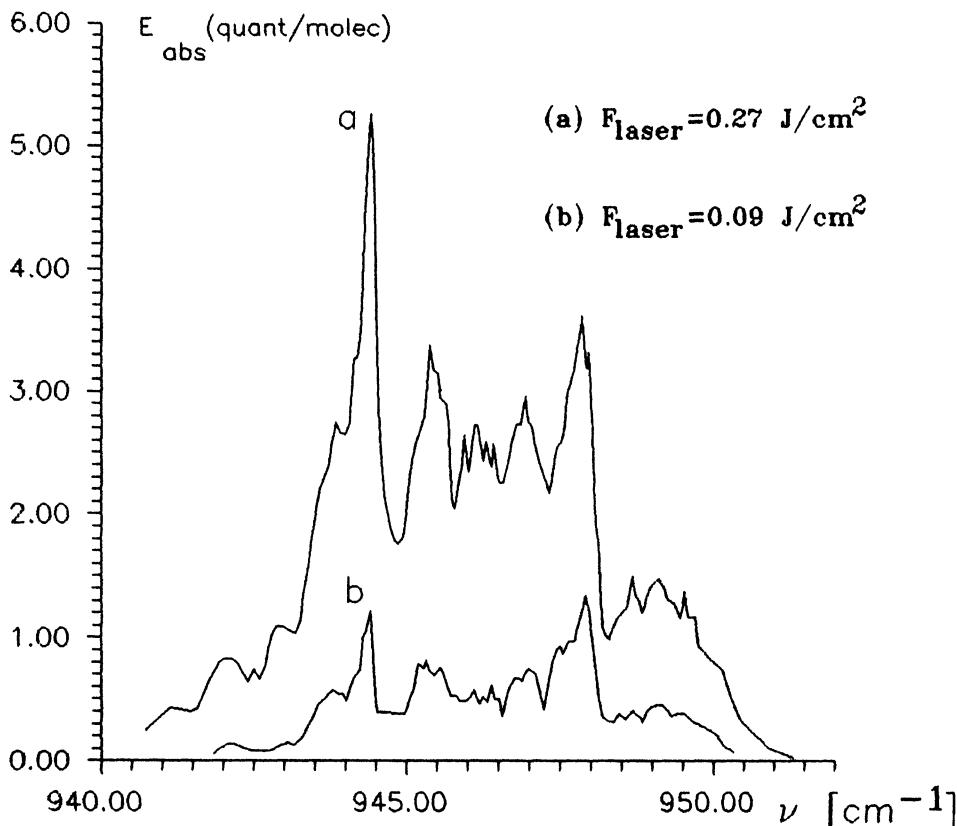


Figure 1 Spectral dependencies of absorbed energy at one frequency excitation of SF_6 .

$\text{SF}_6:\text{Xe} = 1:10$ was 0.3 Torr. The absorbed energy was measured opto-acoustically and calibrated with the help of transmittance measurements.

The spectra reveal a peak of 947.9 cm^{-1} which is easy to assign as Q-branch of fundamental transition ($0\text{A}_{1g}-1\text{F}_{1u}$). The spectra display also the prominent absorption peak at 944.46 cm^{-1} which is due to two photon transition $0\text{A}_{1g}-2\text{A}_{1g}$. Indeed, the excited vibrational states of v_3 mode are split into sublevels due to intramode anharmonic coupling. The $v = 2$ state is split into three sublevels. The anharmonicity constants of v_3 mode of SF_6 are well known from literature.⁷⁻¹⁰ The calculated position of the peak of two photon transition from ground $v = 0\text{ A}_{1g}$ symmetry vibrational state to $v = 2\text{ A}_{1g}$ symmetry sublevel is in a good agreement with observed one. Two other sublevels of E_g and F_{2g} symmetry of $v = 2$ vibrational state are perturbed due to the vibration-rotation coupling. The peaks in the absorption spectra concerned with Q-branches of transitions $0\text{A}_{1g}-2\text{E}_g$ and $0\text{A}_{1g}-2\text{F}_{2g}$ are broadened due to this coupling. Their positions would be 945.8 cm^{-1} (E_g sublevel) and 948.4 cm^{-1} (F_{2g} sublevel) if there were not vibration-rotation coupling. So the broad peaks near 945.41 cm^{-1} and 948.7 cm^{-1} may be assigned as two photon $0\text{A}_{1g}-2\text{E}_g$ and $0\text{A}_{1g}-2\text{F}_{2g}$ transitions.

The two frequency technique was used to investigate spectra of transitions between excited states of v_3 mode of SF_6 . First laser pulse of 4 atm pressure TEA CO_2 laser excited SF_6 molecules. Second laser pulse of continuously tuned high pressure CO_2 laser was used to probe absorption concerned with the excited molecules. The gas mixture $\text{CO}_2:\text{N}_2:\text{He} = 1:1:6$ pressure 4 atm in the first laser provided the range of continuous tuning $\pm 0.25 \text{ cm}^{-1}$ near 10P16 line. The frequency of first pulse was chosen to be 947.9 cm^{-1} in resonance with Q-branch of fundamental transition. The frequency of second pulse was varied in the range $940\text{--}944 \text{ cm}^{-1}$. Both pulses were synchronized with zero time delay. The fluctuations of delay time were $\pm 20 \text{ ns}$. The energy fluence of each pulse was 0.1 J cm^2 . The spectrum is shown in Figure 2. Two peaks in the spectrum were assigned as Q-branches of vibrational transitions $1\text{F}_{1u}\text{--}2\text{A}_{1g}$ and $1\text{F}_{1u}\text{--}2\text{E}_g$ with unresolved rotational structure. The position of $1\text{F}_{1u}\text{--}2\text{A}_{1g}$ peak in the spectrum is 940.5 cm^{-1} and $1\text{F}_{1u}\text{--}2\text{E}_g$ peak is 943.2 cm^{-1} . The shifts of both peaks from fundamental frequency are twice by comparison with the shifts of two photon peaks $0\text{A}_{1g}\text{--}2\text{A}_{1g}$ and $0\text{A}_{1g}\text{--}2\text{E}_g$ in Figure 1. The peak of $1\text{F}_{1u}\text{--}2\text{E}_g$ transition is broad due to rotation-vibration coupling between 2E_g and 2F_{2g} sublevels.

Figure 3 shows the IR multiphoton absorption spectra of CF_3Br investigated at gas pressure 0.3 Torr. The spectrum shown in Figure 3a was investigated at one frequency excitation and published in Reference 11. It proved possible to assign main

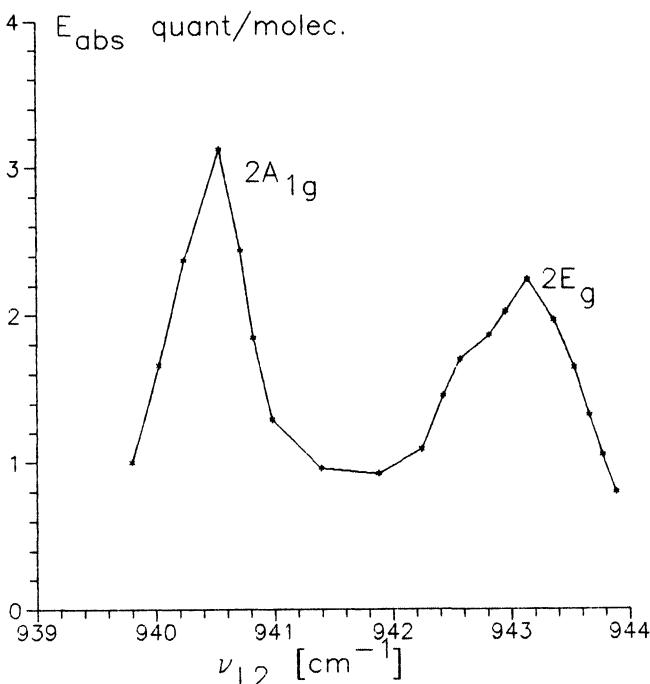


Figure 2 Absorbed energy spectra at two frequency excitation of SF_6 .

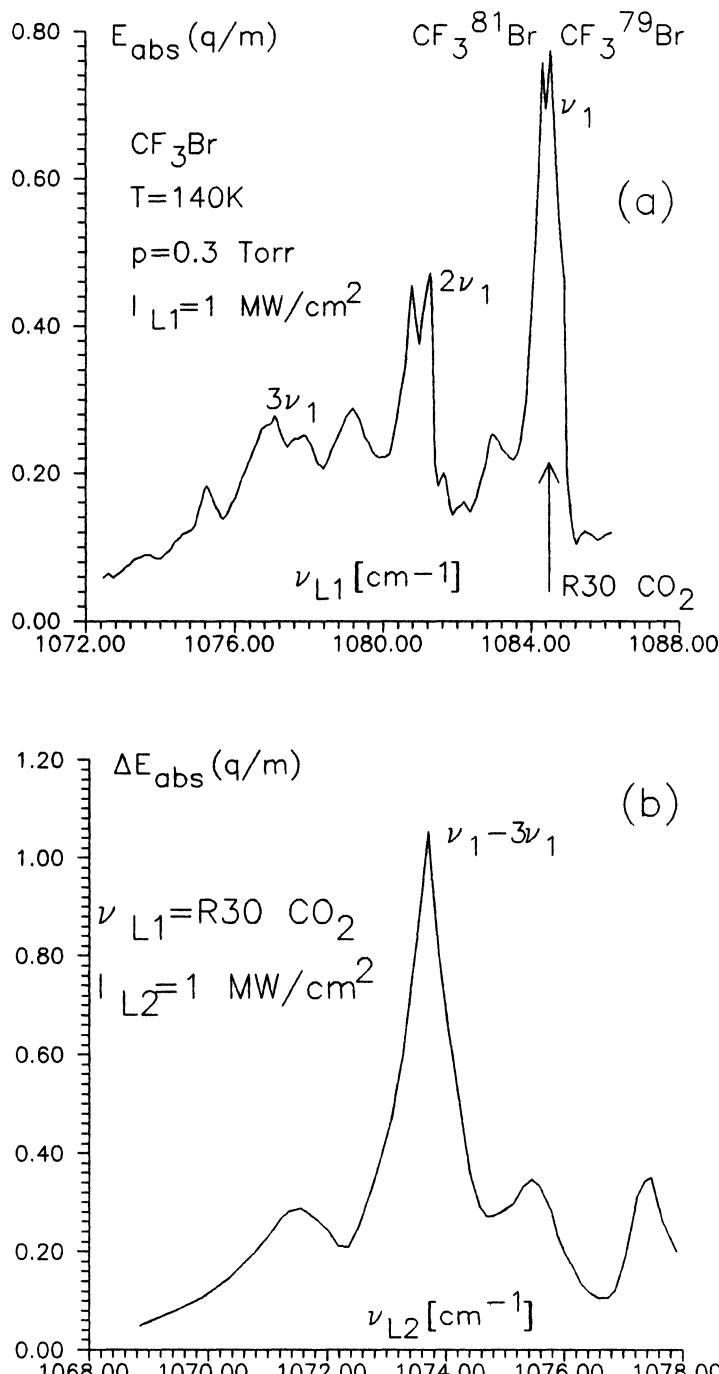


Figure 3 Absorption spectra of CF_3Br . One (a) and two (b) frequency excitation.

peaks in this spectrum. The doublets with lines separated by $\Delta = 0.26 \text{ cm}^{-1}$ are owing to isotopic species $\text{CF}_3^{79}\text{Br}$ and $\text{CF}_3^{81}\text{Br}$. The successive doublets separated by 3.34 cm^{-1} are the peaks of one, two and three photon absorption lines the three photon peak being a weak. Both values are in a good agreement with the isotopic shift of v_1 mode of CF_3Br $\Delta = 0.242 \text{ cm}^{-1}$ and the anharmonicity constant $X_{11} = 3.37 \text{ cm}^{-1}$.¹²⁻¹⁴

Q-branch of fundamental transition of v_1 mode of CF_3Br is in a resonance with 9R30 line of CO_2 laser. Spectrum of Figure 3b shows the result of two frequency experiment when CF_3Br gas was excited by the pulse of atmospheric TEA CO_2 laser operating at 9R30 line and then the absorption spectrum of excited molecules was investigated with continuously tuned CO_2 laser. The two pulses were synchronized with zero delay time. Both TEA CO_2 laser pulse and probing pulse intensities were 1 MW cm^2 . The spectrum shows the peak assigned as two photon transition $1v_1 - 3v_1$. The peak has no noticeable isotopic structure due to selective excitation of one isotopic species by the first laser pulse.

The peaks observed in the IR multiphoton absorption spectra of SF_6 and CF_3Br have a width about 0.3 cm^{-1} . The width of peaks did not depend on laser pulse intensity up to 1 MW cm^2 . These peaks have a fine rotational-vibrational structure which can be observed with resolution of 1 MHz .^{7,8} The observed in our experiments width 0.3 cm^{-1} is due to inhomogeneous broadening. It is clear that one can use these peaks in IR multiphoton excitation spectra to achieve a high selectivity of MPE even in the excitation of molecules of heavy isotopes. The deep cooling of a gas leading to reducing of inhomogeneous broadening may be used to increase the selectivity of excitation. The two frequency excitation has obvious advantage of multiplication this selectivity.

The following experiments were done to investigate the absorption spectra in QC region of polyatomic molecules. The results of these experiments were earlier published in Reference 15. The absorption spectra were investigated by the two frequency technique. SF_6 gas at room temperature was excited by 10P20 TEA CO_2 laser pulse with varied energy fluence in the range $0.5 - 2.5 \text{ J cm}^2$. The linear absorption spectra of molecules excited into quasicontinuum was probed by second laser pulse. To probe linear absorption $^{12}\text{CO}_2$, $^{13}\text{CO}_2$ and NH_3 lasers were used. The spectral region $770 - 950 \text{ cm}^{-1}$ was covered. The absorption cross section σ was measured by transmittance technique. The energy fluence of second pulse was chosen to satisfy the linearity condition and did not exceed 1 mJ/cm^2 . The time delay between two pulses was $1 \mu\text{s}$. The spectral dependencies of σ versus laser frequency are shown in Figure 4 for three levels of excitation of molecules by first laser pulse: $E_{\text{abs}} = 8.4$, 13.4, and 25 quanta per molecule.

There is only alone structureless peak in the spectra. This peak is shifted due to anharmonicity to the long wave side from the fundamental transition of v_3 mode. Both shift and width of a peak rise linearly with increasing of absorbed energy. In fact observed peak is due to overlapping of the spectra of successive transitions in QC. The changes in the peak position and width are due to changes in the population distribution in QC. A simple and reasonable model make it possible to estimate the characteristics of individual transition in QC. Let assume that line shape of individual

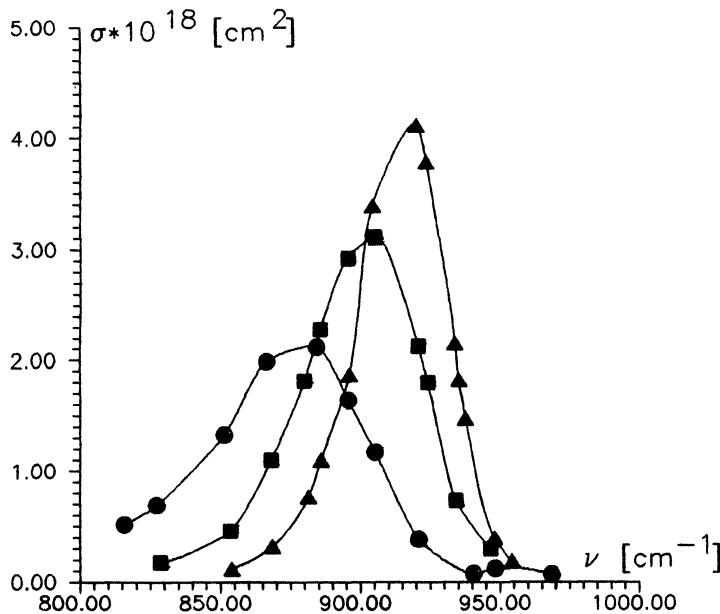


Figure 4 Linear absorption spectra of SF₆ in quasicontinuum. E_{abs} = 8.4 q/m—triangles; E_{abs} = 13.4 q/m—squares; E_{abs} = 25 q/m—circles.

transition in QC has Lorentz profile:

$$\sigma(v, v \rightarrow v + 1) = \frac{A_{01} X_2 v}{\pi [(v - v_0 - X_1 v)^2 + (X_2 v)^2]} \quad (1)$$

where A₀₁ is integral cross section of vibrational mode; v₀ is frequency of fundamental transition; shift X₁v and half-width X₂v increase linearly with increasing of the number v of the level in the ladder of states populated by laser pulse. Let population distribution over v is thermal like:

$$n(v) = v^{s-1} \exp(-sv/\Theta)/[\Theta(s-1)!] \quad (2)$$

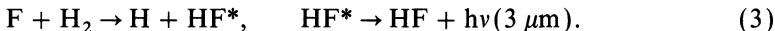
where s is the number of vibrational degrees of freedom in QC; Θ = kT/hcv, T being the effective temperature of the vibrational distribution. The modeling of observed spectra yields A₀₁ ≈ 1.7 · 10⁻¹⁶ cm, s ≈ 10, X₁ ≈ -3.1 cm⁻¹, X₂ ≈ 0.4 cm⁻¹. The first conclusion is that measured integral cross section is equal to that of the fundamental transition.¹⁶ The number of degrees of freedom s involved in QC formation is less than the total number of vibrational degrees of freedom in SF₆ s_{total} = 15. Apparently this fact can be explained by so called “freezing” of high frequency modes participating in QC formation. So the statistical weight of high frequency modes decreases when kT is less than hcv. The very interesting result is that broadening X₂v of transitions in QC is small by comparison with the shift X₁v.

DISSOCIATION SPECTROSCOPY

The spectral structure of discrete level excitation appears in the dissociation spectra.¹⁷ This fact is of great importance for the selectivity of multiphoton dissociation of polyatomic molecules.

The experiments on dissociation spectroscopy were carried out with gases cooled in supersonic jet. We investigated IR MPD spectra of SF₆ and OsO₄ molecules. The gasdynamic cooling makes it possible to obtain low rotational temperature and thus reduce the inhomogeneous broadening of multiphoton transitions. The rotational temperature of molecules cooled in supersonic jet was estimated with diode spectroscopy measurements to be T_{rot} ≈ 30 K and vibrational temperature T_{vib} ≈ 100 K.

The dissociation yield was measured by the luminescence technique. The products of SF₆ MPD process are SF₅ radicals and F atoms. The chemical reaction of F atoms with hydrogen molecules was used to obtain HF-luminescence signal proportional to the dissociation yield of F atoms:



The dissociation of OsO₄ molecules is accompanied with visible luminescence.¹⁸

The dissociation of SF₆ molecules was performed with the help of three CO₂ laser pulses. Two pulses were used to study the process of DL excitation in the course of MPD. Third pulse was applied to dissociate molecules excited into the quasicontinuum. The frequency of first pulse was close to the fundamental frequency of v₃ of SF₆. The frequency of second pulse was chosen to be in resonance with transitions between excited states of v₃ mode. The frequency of third pulse was shifted to the longwave side from fundamental v₃ mode transition to optimize the excitation process in QC region. It was possible to investigate as the spectra of multiphoton transitions from ground vibrational state and the spectra of transitions between excited vibrational states.

Figure 5 shows the dissociation spectra of SF₆. The stagnation pressure of SF₆:H₂ = 1:20 mixture in the nozzle receiver chamber was 250 Torr. The pulsed slit nozzle dimensions were 0.03 × 3 cm. The nozzle chamber was pumped out to pressure 10⁻⁶ Torr. The PbS detector was used to measure HF luminescence signal. Two TEA CO₂ lasers and one continuously tuned high pressure CO₂ laser were utilized in experiments. Three laser pulses were synchronized. Time delay between first and second pulses was chosen to be zero the fluctuations of time delay being in the range ± 20 ns. The time delay of third pulse was 500 ns. Third laser operated with ¹³CO₂ gas mixture to obtain laser pulse frequency near 900 cm⁻¹ that is optimal in the course of SF₆ excitation in QC region.

Two combinations of laser frequencies were used to investigate DL spectra. First combination with TEA CO₂ lasers operating at 10P34 line of ¹²CO₂ (v_{L2} = 931 cm⁻¹) and 10P30 of ¹³CO₂ (v_{L3} = 888 cm⁻¹) was chosen to investigate with continuously tuned laser pulse the spectra of multiphoton transitions of SF₆ from the ground vibrational state to the excited states. Second combination with two TEA CO₂ lasers operating at 947.9 cm⁻¹ near 10P16 of ¹²CO₂ and 10P12 line of ¹³CO₂

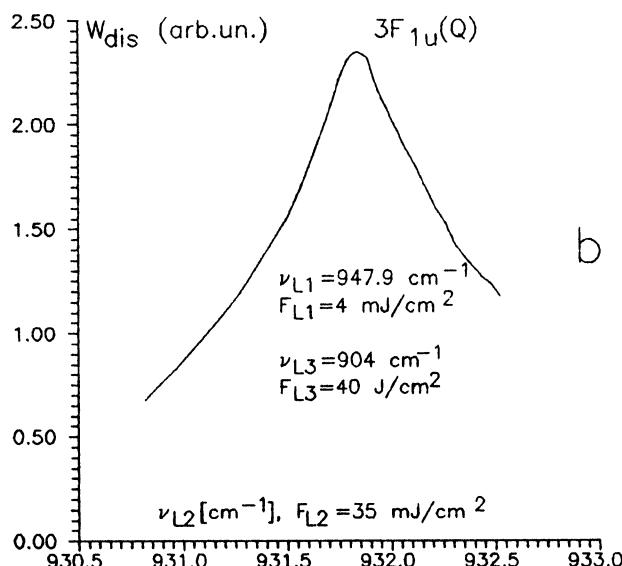
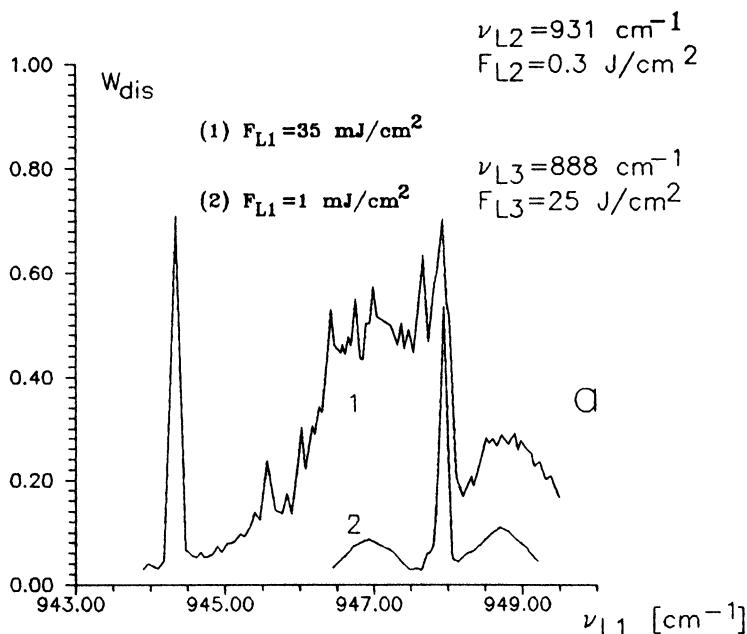


Figure 5 Dissociation spectra of SF_6 with first laser pulse tuned (a) and second laser pulse tuned (b).

($v_{L3} = 904 \text{ cm}^{-1}$) were chosen to investigate with continuously tuned high pressure laser pulse the spectra of transitions between excited states of SF₆. Increasing of the energy fluences of three pulses resulted in a saturation of HF-luminescence signal. The saturation limit of HF-signal was assumed to correspond to 100% dissociation yield.

Figure 5a displays results obtained with first combination of laser pulse frequencies. The most striking result is that the dissociation spectrum reveals the structure of the fundamental vibrational transition of v_3 mode of SF₆ at energy fluence of continuously tuned laser pulse 1 mJ/cm². It became possible to observe this spectrum due to optimal choose of frequencies of second and third laser pulses. Increasing of first laser pulse energy fluence leads to the appearance of two photon peaks in the dissociation spectrum. These peaks are seen in the spectrum obtained at first laser pulse energy fluence 35 mJ/cm². The most prominent peak is those concerned with two photon transition 0A_{1g}-2A_{1g} at frequency 944.46 cm⁻¹. It is very important from isotope separation point of view that the dissociation yield at maximum is close to 100% for both spectra.

The cooling of SF₆ in supersonic jet resulted in the narrowing of two photon peaks. Indeed, the width of 0A_{1g}-2A_{1g} peak that was measured with resolution $\pm 0.03 \text{ cm}^{-1}$ is not more than 0.1 cm⁻¹ at cooling in supersonic jet. The width of the same peak measured in the absorption spectra obtained at T = 140 K is approximately 0.3 cm⁻¹. Low rotational temperature results in the reducing of a width of other Q-branches of two photon transitions as well. The main reason is concerned with the depopulation of rotational states with high values of rotational quantum number J at low rotational temperature. Thus the inhomogeneous broadening due to rotation-vibration coupling in the v = 2 vibrational state is reduced. Q-branch of two photon transition 0A_{1g}-2E_g is seen in the dissociation spectra as a contrast and narrow peak with frequency position 945.6 cm⁻¹. Q-branch of two photon transition 0A_{1g}-2F_{2g} is not seen in the spectrum as narrow peak. Two reasons can be assumed to explain this fact. First is that it needs cooling to the temperatures less than 30 K to reduce the inhomogeneous width of this Q-branch. Second is that Q-branch of three photon transition 0A_{1g}-3A_{2u} which can be observed at 948.6 cm⁻¹ overlaps this two photon Q-branch that results in the broad structureless peak near 949 cm⁻¹ which is seen in the dissociation spectra. The appearance of some peaks in the region 946–947 cm⁻¹ which could not be assigned as two photon is the evidence that there are multiphoton transitions (more than two photon) with small detuning off fundamental v_3 frequency in the dissociation spectrum.

Figure 5b displays results with second combination of laser frequencies. First 4 atm TEA CO₂ laser pulse was in the resonance with Q-branch of fundamental transition. Its frequency was tuned to 947.9 cm⁻¹. The pulse of continuously tunable high pressure CO₂ laser was used as second pulse. Its frequency was varied in the region 931–933 cm⁻¹. Shown in Figure 6 is a contrast peak observed near the frequency 931.8 cm⁻¹ in the dissociation spectrum. This peak is obviously concerned with transitions between excited states of v_3 mode of SF₆. Indeed, the combination of the two frequencies $v_{L1} = 947.9 \text{ cm}^{-1}$ and $v_{L2} = 931.8 \text{ cm}^{-1}$ is in resonance with Q-branch of two photon transition 1F_{1u}-3F_{1u} as it follows from data on 3v₃ overtone

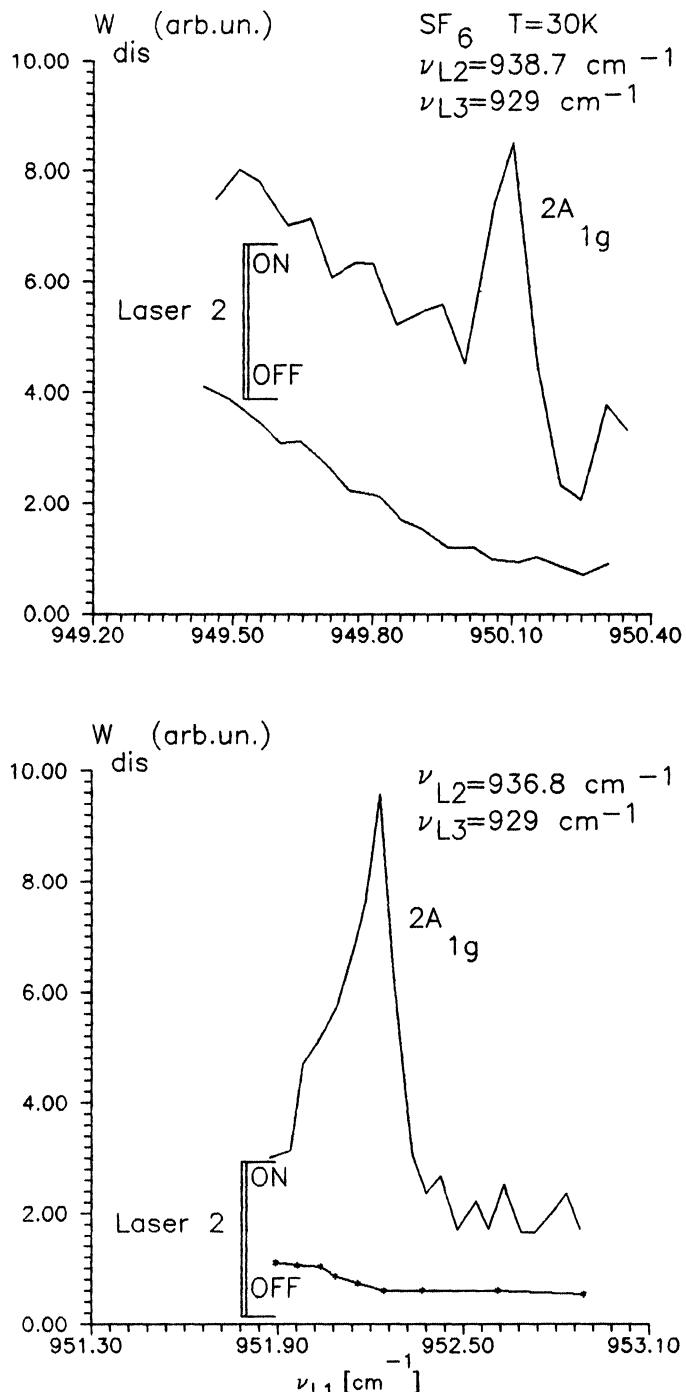


Figure 6 Bichromatic excitation of SF_6 .

spectra.⁹ Calculations of v_3 mode ladder show (see below) that at the same time v_{L2} is in resonance with Q-branch of one photon transitions $3F_{1u} - 4A_{1g}$ and $3F_{1u} - 4E_g$ (energy gap between vibrational sublevels A_{1g} and E_g of $v = 4$ is very small). So this combination is an optimal one for excitation from $v = 1$ state of v_3 up to $v = 4$ state.

Thus, experiments on three frequency multiphoton dissociation of SF_6 cooled in supersonic jet showed that there are narrow resonances in the IR multiphoton spectra concerned with multiphoton transitions in DL ladder. It is possible to take advantage of these resonances to investigate the structure of vibrational-rotational spectra of excited vibrational states of polyatomic molecules. These resonances demonstrate a way to reach high selectivity and high efficiency of isotope separation by means of MPD via multifrequency laser excitation.

BICHROMATIC EXCITATION

Employing of two frequencies in the course of DL excitation make it possible to perform a bichromatic (two color) excitation of two photon transitions. Bichromatic excitation of two photon transitions with the help of two simultaneously applied laser pulses may be useful from the IR multiphoton spectroscopy point of view. Indeed, if a line tuned lasers are used for DL excitation, one deals with limited number N of these lines. Employing of bichromatic excitation make it possible to chose some of available $N \cdot (N + 1)/2$ combinations which are in resonance with two photon transitions of interest. Another advantage is concerned with the possibility to investigate IR multiphoton spectra anaccessible with one frequency DL excitation.

Figure 6 shows dissociation spectra of SF_6 at bichromatic excitation of discrete levels. First and second laser pulses were synchronized with zero time delay. Those frequencies v_{L1} and v_{L2} were chosen to satisfy two photon resonance condition:

$$v_{L1} + v_{L2} = (E(v = 2, A_{1g}) - E(v = 0, A_{1g})) / hc \quad (4)$$

Two photon peak in the dissociation spectra obtained by varying the frequency of first pulse throughout appropriate region was observed for two frequencies of second pulse. Two frequencies of second pulse were 938.7 cm^{-1} (10P26) and 936.8 cm^{-1} (10P28). Frequency of third pulse was 929 cm^{-1} (10P36). Intensities of three pulses were ~ 2 , ~ 0.2 and $\sim 70 \text{ MW/cm}^2$ respectively. The difference between the spectra with second pulse on/off demonstrates that observed peak is due to bichromatic excitation. The altering of second pulse frequency results in changing of peak position in accordance with relation (4) that Figure 6a and Figure 6b demonstrate. The observed shift of the peak satisfies (4) relation. This is a convincing evidence that this peak is due to two photon transition.

Figure 7 shows the spectrum of bichromatic excitation of OSO_4 cooled in a supersonic jet. The mixture of $OsO_4:He = 1:250$ was cooled down to rotational temperature $T_{rot} = 30 \text{ K}$. The frequency of first pulse v_{L1} was varied throughout the region $940 \text{ cm}^{-1} - 955 \text{ cm}^{-1}$. The frequency of second pulse was $v_{L2} = 969.1 \text{ cm}^{-1}$ (10R10). The spectrum is represented as the dependence of the ratio of luminescence signal with the second pulse on to the signal with second pulse off versus reduced

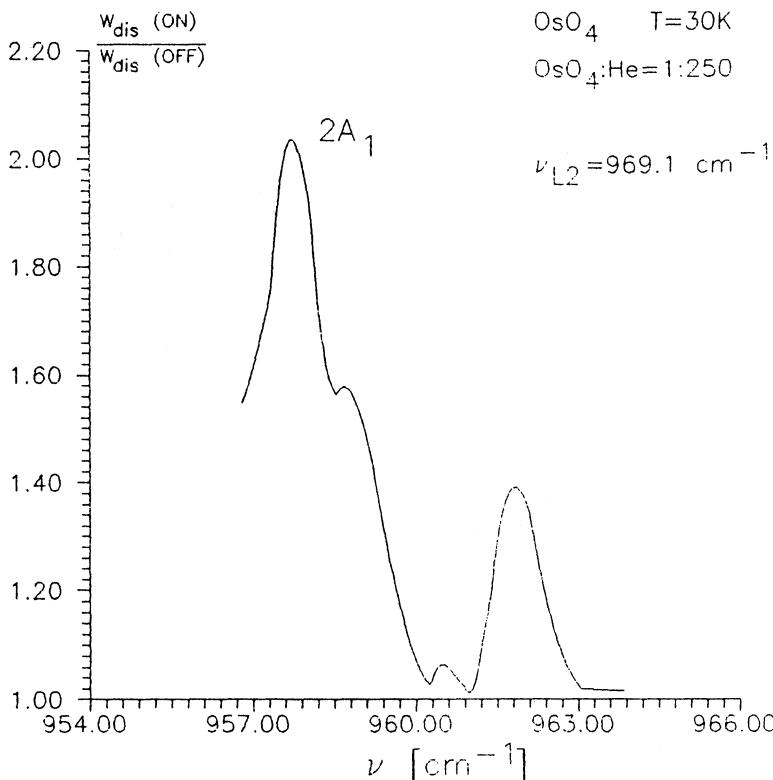


Figure 7 Bichromatic excitation of OsO_4 .

frequency $\nu = (\nu_{L1} + \nu_{L2})/2$. The reduced frequency was tuned from 954.6 cm^{-1} to 962.1 cm^{-1} . This frequency region lies just between P and R generation branches of common $^{12}\text{CO}_2$ laser and is anaccessible for one frequency study of multiphoton transition in ν_3 mode of OsO_4 . The position of two photon peak in the observed spectrum is in a good agreement with the frequency of first overtone of ν_3 of OsO_4 , measured in Reference 19. It is important from the isotope selective dissociation point of view that OSO_4 is an example of a molecule with heavy atom. The observed spectrum demonstrates therefore the availability of selective dissociation of molecules with heavy atom or with small isotopic shift of vibrational frequency.

NONLINEAR SPECTROSCOPY TECHNIQUES

Two nonlinear techniques as degenerate four wave mixing and third harmonic generation were utilized to investigate the excited vibrational state spectra of polyatomic molecules. These techniques have an advantage in the coarse of investigation of second or third vibrational level. As absorption and dissociation

spectroscopy yields the spectra with overlapping peaks of one, two and more photon transitions. Nonlinear spectroscopy makes it possible to observe only spectra concerned with two or three photon transitions. So it has an advantage in the investigation of spectra of certain vibrational level.

Degenerate four wave mixing is a process of coherent generation of light wave when pumping of a media by three coherent light waves with all waves being of the same frequency. To satisfy coherence condition the wave vectors of four waves must obey the relation

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{k}_4. \quad (5)$$

This relation means that irradiating of a media with three waves in such a manner that two of them (pump waves) are propagating in opposite directions ($\vec{k}_1 = -\vec{k}_2$) results in a generation of fourth wave (signal wave) propagating in opposite direction to third (probe) wave: $\vec{k}_3 = -\vec{k}_4$. So it is very easy to discriminate the signal wave in experiment.

Resonant interaction of laser fields with molecules makes it possible to perform degenerate four wave mixing spectroscopy (DFWMS) of first and second excited vibrational states of IR active modes. In the case of resonant interaction of laser fields with IR active mode two ways of DFWM are possible.^{20,21} These ways are shown in the energy diagrams of Figure 8.

In a first case shown in Figure 8 the polarization is defined by the relation

$$\vec{P}_4 = \chi_1 \cdot (\vec{E}_1 \cdot \vec{E}_3^*) \cdot \vec{E}_2 \quad (6)$$

where \vec{E}_1 are amplitudes of pump and probe fields, \vec{P}_4 is polarization of a molecule which results in generation of signal wave, χ_1 is nonlinear susceptibility of a molecule which depends on the laser frequency in a resonant manner and is proportional to

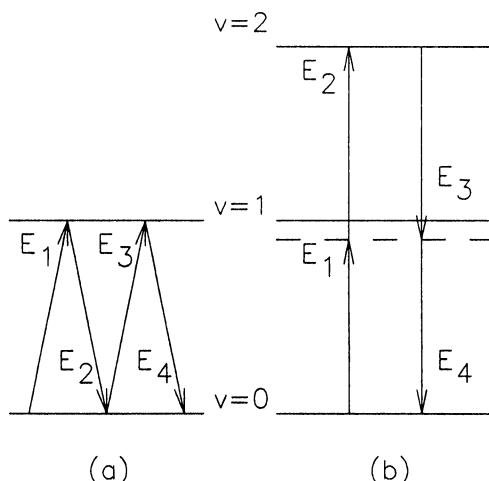


Figure 8 Diagram of level pumping in the process of DFWM.

$[(\nu - \nu_{01} + i\gamma_{01})]^{-1}$, ν_{01} is frequency of one photon transition, γ_{01} is line width of the transition.

In a second case shown in Figure 8 the polarization is defined by the relation

$$\vec{P}_4 = \chi_2 \cdot (\vec{E}_1 \cdot \vec{E}_2) \cdot \vec{E}_3^* \quad (7)$$

where nonlinear susceptibility χ_2 resonantly depends on the laser frequency and is proportional to $[(2\nu - \nu_{02} + i\gamma_{02})]^{-1}$ near the frequency of two photon transition ν_{02} , γ_{02} is line width of this transition.

Employing of linearly polarized laser fields with polarization of probe wave perpendicular to polarization of pump waves make it possible to realize the generation of signal wave by second way. As result it is possible to observe the spectra of two photon transition by means of DFWMS.

Figure 9 shows the DFWM spectrum of SF₆ cooled in a cell at temperature T = 140 K. Three waves were produced from one laser pulse by splitting of laser beam with germanium plate (one transmitted and two reflected). The angle between pump and probe waves was 3°. The pump wave intensions were equal. Intensity of probe wave was $I_{\text{probe}} = 0.1 \cdot I_{\text{pump}}$. Reflection index of weak probe laser pulse was measured. The spectrum reveals peaks of two photon transitions 0A_{1g}-2A_{1g} (944.46 cm⁻¹), 0A_{1g}-2E_g (945.6 cm⁻¹), 0A_{1g}-2F_{2g} (peaks near 948 cm⁻¹).

The DFWM spectrum has more simple structure than the absorption spectrum

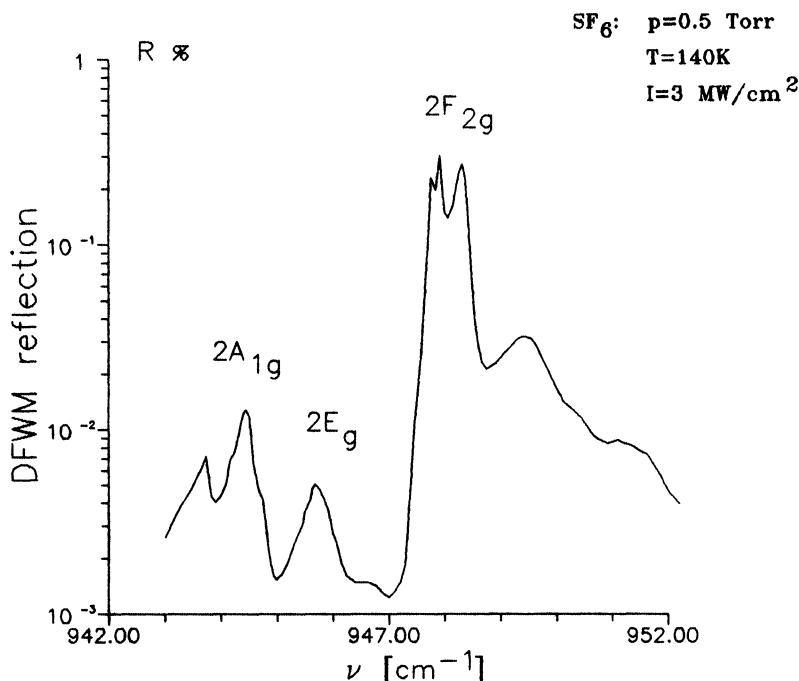


Figure 9 DFWM spectrum of SF₆.

obtained at similar conditions (see Figure 1). There are not peaks due to multiphoton transitions with order of transition more than two in DFWM spectra in contrast to absorption spectra at the same temperature $T = 140$ K. So it follows that complex structure in the absorption spectra which was observed in the spectral range $946\text{--}947\text{ cm}^{-1}$ is due to three photon transitions and maybe to four photon one.

Another nonlinear IR multiphoton spectroscopy technique utilized to investigate multiphoton spectra is third harmonic generation spectroscopy (THGS). The polarization of molecules resonantly pumped by laser field has a third harmonic contribution which is sensitive to the resonances of laser field with the multiphoton transitions in pumped vibrational mode:

$$\vec{P}_{3v} = \chi_{3v} \cdot (\vec{E} \cdot \vec{E}) \cdot \vec{E} \quad (8)$$

with $\chi_{3v} \sim [(v - v_{01}) \cdot (2 \cdot v - v_{02}) \cdot (3 \cdot v - v_{03})]^{-1}$; v_{01} , v_{02} and v_{03} are frequencies of one, two and three photon transition. Resonant enhancement of nonlinear susceptibility makes it possible to conduct the investigation of the spectra of excited vibrational states by means of THGS.

The THG spectrum of SF_6 cooled in supersonic jet was obtained with the help of continuously tuned CO_2 laser. The $10\text{ }\mu\text{m}$ laser radiation transmitted through the jet was filtered out and $3\text{ }\mu\text{m}$ third harmonic signal was measured by InSb detector. Figure 10 shows THG spectrum of SF_6 at $T = 30$ K obtained at laser intensity

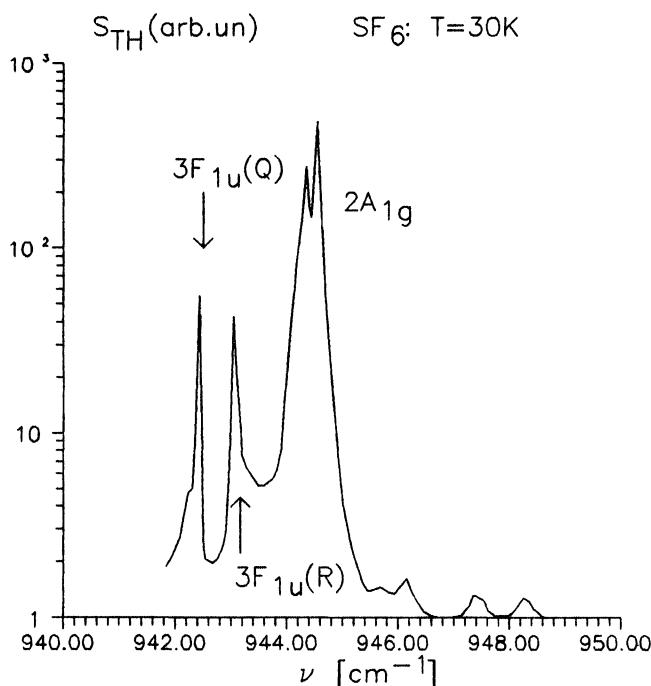


Figure 10 THG spectra of SF_6 .

1 MW/cm². There are two new peaks in the spectrum by comparison with the dissociation spectrum obtained at similar conditions (see Figure 5). These peaks have frequencies 942.2 cm⁻¹ and 943.03 cm⁻¹. They are shifted to the long wave side from the two photon peak at 944.46 cm⁻¹. The latter is split due to saturation of two photon transition. The dip was observed in the two photon peak when laser frequency was exactly in resonance with this transition. These new peaks can be assigned as Q and R rotational branches of three photon transition 0A_{1g}-3F_{1u} as it follows from the measurements of second overtone spectra of SF₆.⁹

The nonlinear spectroscopy techniques are the complimentary to the absorption and dissociation spectroscopy of excited vibrational states of polyatomic molecules. These techniques give a reliable assignment of observed peaks as two or three photon transition. The THG spectroscopy is more straightforward in the observation of spectra of third vibrational state of a vibrational mode by comparison with the absorption or dissociation spectroscopy which needs to use two frequency technique to do it.

COMPUTER SIMULATION OF MOLECULAR SPECTRA

Computer calculations of the excited vibrational state spectra are of great interest for the investigation of excited states of molecules. The calculations make it possible to extract a spectroscopic parameters of a molecule from the spectra observed in the experiment. The comprehensive information about spectroscopic parameters of a molecule can be used for subsequent calculations of molecular spectra both linear and multiphoton. So these calculations can be used to simulate the spectra of interest and to predict the behavior of a molecule in an intense laser field.

In this section the results are presented concerned with the calculation of excited vibrational state spectra of spherical top molecules. The spherical top molecules are of great interest from the isotope selective dissociation point of view. The wide known example is SF₆ molecule. Multiphoton dissociation of SF₆ was investigated in a lot of laboratories. So it is possible to compare the results of calculations with experimental one.

The program package was developed to calculate the rotational-vibrational spectra of excited vibrational states of IR active modes of spherical top molecules XY₄(T_d) and XY₆(O_h) and dipole moments of transitions between excited vibrational states. The Hamiltonian to fourth order of approximation for v₃ mode is given by the following formula^{22,23}:

$$\begin{aligned} \hat{H} = & v_3 \cdot v + B \cdot J \cdot (J+1) + (B\zeta) \cdot [R \cdot (R+1) - J \cdot (J+1) - 1 \cdot (1+1)] \\ & + X_{33} \cdot v \cdot (v-1) + G_{33} \cdot [1 \cdot (1+1) - 2 \cdot v] + T_{33} \cdot \sqrt{120} \cdot \hat{T}^{404} \\ & + D_s \cdot [J \cdot (J+1)]^2 + Z_{3s} \cdot \sqrt{5} \cdot \hat{T}^{220} \\ & + \sqrt{120} (Z_{3t} \hat{T}^{224} + D_t \hat{T}^{044} + F_{3t} \hat{T}^{134} + N_{333t} \hat{T}^{313}) \end{aligned} \quad (9)$$

where v is vibrational quantum number, J is quantum number of a total angular

moment, l is quantum number of a vibrational angular moment, R is quantum number of a vector formed by \vec{J} and \vec{I} according to subtraction rule $\vec{R} = \vec{J} - \vec{I}$; rotational parameters of the Hamiltonian are defined by relations: $B = B_0 + v \cdot Y_3$ is rotational constant of vibrational state, $(B\zeta) = (B\zeta)_0 - M_{33} \cdot v - F_{3s} \cdot (J + 1)/2$ is Coriolis parameter for certain vibrational-rotational state. The notation of tensor operators \hat{T}^{nmk} is given in the form known from Reference 24. In this notation the operator of dipole interaction between field and the dipole moment of vibrational mode is

$$\vec{E} \cdot \vec{d} = -\sqrt{3} d_{01} E \cdot \hat{T}^{110} \quad (10)$$

where d_{01} is dipole moment of a fundamental transition of a mode; E is amplitude of light field; the scalar product results in tensor operator \hat{T}^{110} . The Hamiltonian (9) do not take into account the sextic intramode anharmonicity term which contribution is of fourth order and has nonzero matrix elements in vibrational states $v \geq 3$. The corresponding term in the Hamiltonian of IR active modes of spherical top molecules was analyzed in Reference 25:

$$\begin{aligned} \hat{H}_6 &= \delta X_{33} v(v-1)(v-2) + \delta G_{33}[l(l+1)-2v](v-2) \\ &\quad + \sqrt{120} \delta T_{33} \hat{T}^{404} + T_{433} \hat{P}^4 + T_{633} \hat{T}^{66} \end{aligned} \quad (11)$$

where five constants of sextic anharmonicity are defined and two tensor operators \hat{P}^4 and \hat{T}^{66} introduced in Reference 25 are used. The sextic anharmonicity term was taken into account when calculating the excited state spectra.

Shown in Figure 11 are the results of calculations for Q branches of transitions $1F_{1u}-2A_{1g}$ and $1F_{1u}-2E_g$ in comparison with experimental spectra observed in Reference 10. These plots demonstrate that both frequency position and intensity of lines in calculated spectra are in good agreement with experimental one. The spectroscopic parameters known from the spectroscopic study of fundamental transition of v_3 of SF_6 ²⁶ were used in the calculations. Constants X_{33} , G_{33} , T_{33} were fitted to reach an agreement between experimental and calculated spectra. These constants were found to be:

$$X_{33} = -1.7468(5), \quad G_{33} = 0.9262(2), \quad T_{33} = -0.2487(1) \text{ cm}^{-1}.$$

This set of quartic anharmonicity constants differs from that found in Reference 9 where the spectrum of overtone $0-3v_3$ was analyzed. The difference is due to sextic anharmonicity constants of v_3 mode which was not included in the fit in Reference 9. So the comparison of quartic anharmonicity constants found in this work with those found in $0-3v_3$ analysis gives a set of sextic anharmonicity constants:

$$\delta X_{33} = 4.2 \cdot 10^{-3}, \quad \delta G_{33} = -7.2 \cdot 10^{-3}, \quad \delta T_{33} = 2.35 \cdot 10^{-3} \text{ cm}^{-1}$$

with zero values at T_{433} and T_{633} . The values of these constants show that it is necessary to include the sextic anharmonicity terms in the Hamiltonian of v_3 mode to calculate the spectra of excited states with 10^{-3} cm^{-1} accuracy. Indeed, the contribution of sextic anharmonicity to the energy of $v = 3$ state has the order of magnitude 10^{-2} cm^{-1} and for $v = 6$ state the contribution is about 0.5 cm^{-1} .

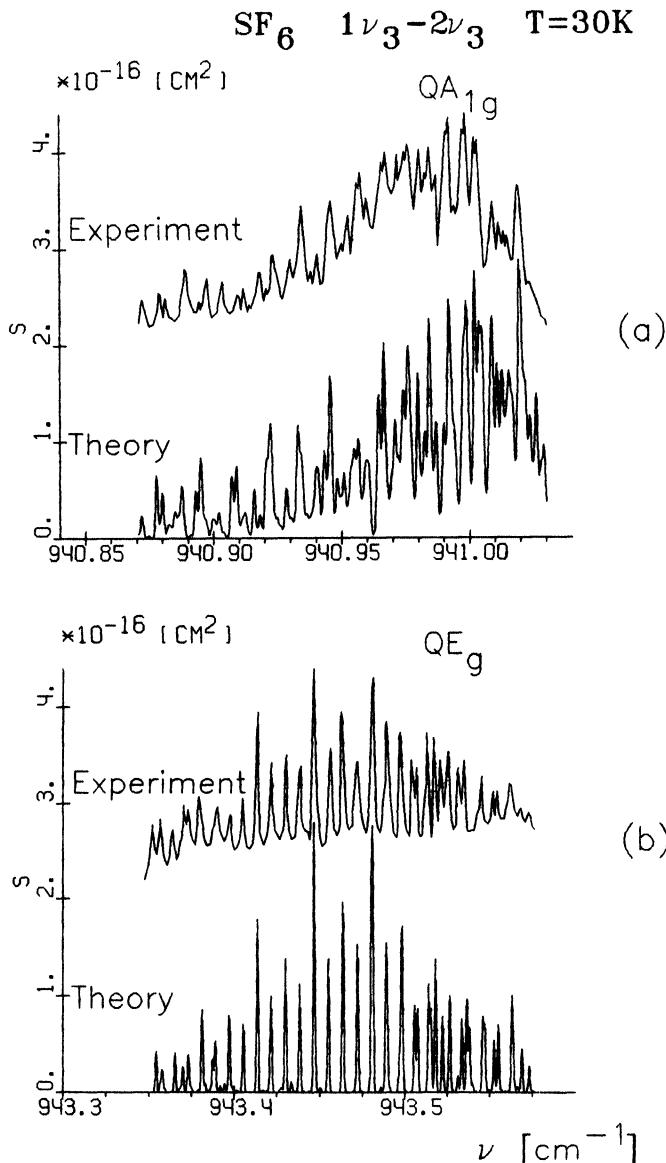


Figure 11 High resolution spectra of transitions $1F_{1u} - 2A_{1g}$ (a) and $1F_{1u} - 2E_g$ (b). Upper curve—experimental data from Reference 10, lower curve—calculated data.

The set of molecular spectroscopic constants found in the coarse of analysis of $1\nu_3 - 2\nu_3$ spectra was used to calculate rotational-vibrational lines of $2\nu_3 - 3\nu_3$ transition of SF_6 . Some of them were observed in Reference 10. Standard deviation between calculated and measured frequencies of the lines was found to be better than 10^{-3} cm^{-1} . Thus, it demonstrates that this set of constants can be used to calculate

the excited vibrational-rotational spectra of excited states of v_3 of SF₆ with accuracy about 10^{-3} cm⁻¹. However, there is a problem of breaking of the Hamiltonian of isolated mode (9) due to anharmonic coupling of v_3 with other vibrational states of molecule. It is this coupling that results in mode mixing and QC formation. So if the energy deposited in the molecule is more than boundary between DL region and QC the Hamiltonian (9) is not valid to describe the spectra of v_3 excited states. In SF₆ this boundary was found to be near $v = 6$ level of v_3 mode.²⁷ So the Hamiltonian (9) is likely valid to calculate the spectra up to $v = 6$ of v_3 .

Detailed agreement between experimental and calculated spectra makes it possible to restore full linear spectra of transitions between excited vibrational states. The survey linear spectra of successive one photon transitions in the v_3 ladder of SF₆ $v = 0 \rightarrow v = 1$, $v = 1 \rightarrow v = 2$, $v = 2 \rightarrow v = 3$ and $v = 3 \rightarrow v = 4$ were calculated with the help of the developed program package. To smooth the detailed structure the line shape of individual rotational-vibrational transition was taken to be lorentzian with FWHM 0.05 cm⁻¹. The spectra calculated at rotational temperature T = 30 K are shown in Figure 12 and can be considered as computer restoration of full linear absorption spectra of transitions between excited vibrational states with deliberate reduced resolution. The spectra visualize that anharmonic and rotation-vibration coupling in the degenerate v_3 mode results in a great broadening of the spectra of transitions between excited vibrational states in contrast to the ordinary anharmonic shift of the spectrum due to anharmonicity in the case of one dimensional oscillator. This broadening makes it possible to overcome the detuning owing to anharmonicity in the coarse of resonant excitation of v_3 mode at fixed frequency of pumping radiation. Indeed, the absorption cross section of $v = 3 \rightarrow v = 4$ transition in the frequency region of fundamental transition is not zero and reaches 10^{-17} cm² order of magnitude. The calculated spectra reveal also the narrow peaks due to overlapping of many rotational lines as in Q-branches and in other rotational branches of vibrational transitions. Q-branches of one photon transitions $3F_{1u} - 4A_{1g}$ and $3F_{1u} - 4E_g$ near 931.8 cm⁻¹ (energy gap between vibrational sublevels A_{1g} and E_g of $v = 4$ is very small) were observed in the three frequency dissociation spectrum (see above Figure 5b).

Next program package was created to simulate the excitation of molecules by intense IR radiation. The calculations of spectral dependencies of absorbed energy were based on a simple model. One and two photon transitions from ground vibrational state were taken into account. The subsequent excitation of molecules from second vibrational state of v_3 to excited states was described by successive one photon transitions with phenomenological absorption cross section given by relation (1). The pulse shape was taken to be rectangular.

The calculations were based on the following model. Interaction of laser pulse with discrete levels was described by Schrödinger equation:

$$i \cdot \hbar \cdot \psi = H \cdot \psi + \vec{J} \cdot \vec{d} \cdot \cos(\omega \cdot t) \cdot \psi \quad (12)$$

The set of eigenvalues $\{E_{v,k}\}$ of Hamiltonian H was calculated by first program package with H taken in form (9); v is vibrational quantum number, $E_{v,k} \approx v \cdot \hbar \cdot \omega$; k designates additional quantum numbers. Let $|v, k\rangle$ be eigenfunctions corresponding

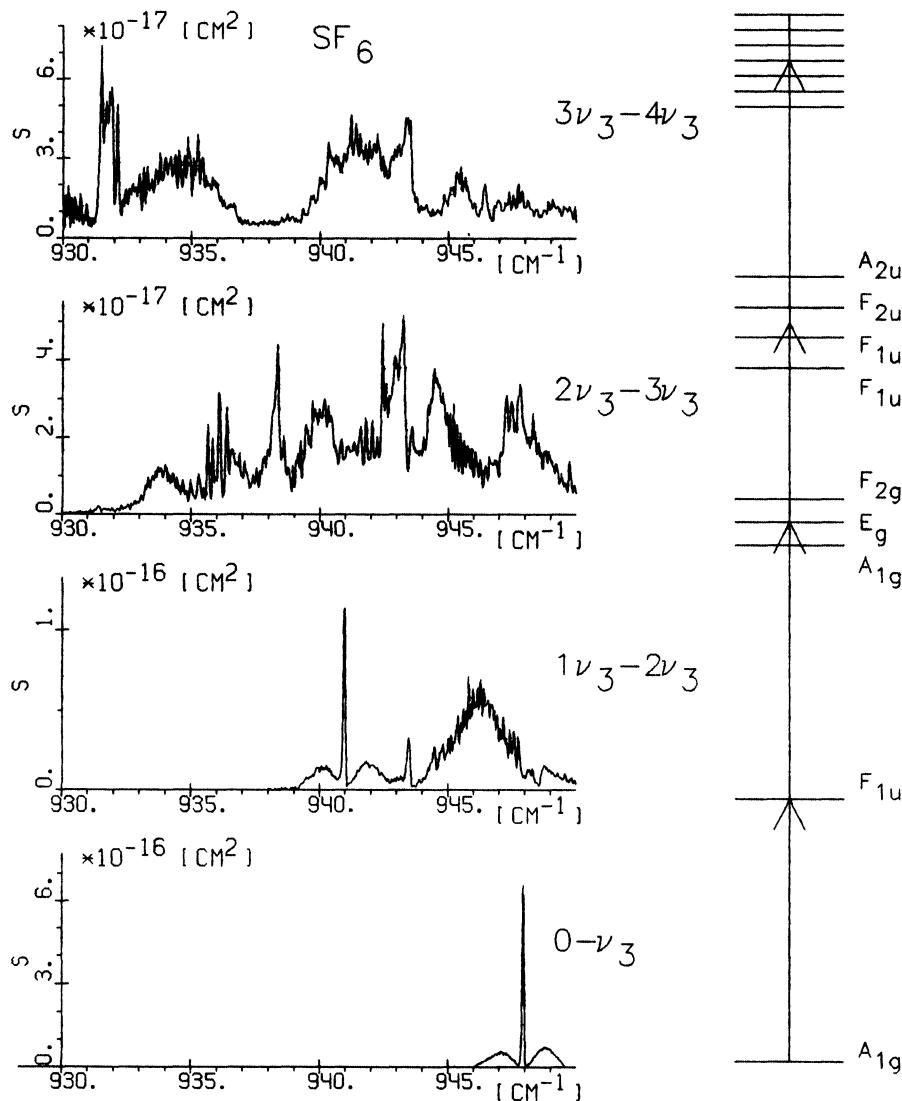


Figure 12 Survey spectra of successive one photon transitions in v_3 ladder of SF_6 .

to $E_{v,k}$ then ψ is represented by

$$\psi = \sum_{v,k} a_{vk} \cdot |v, k\rangle \quad (13)$$

From (12) we get equations for $a_{v,k}$

$$i \cdot \hbar \cdot \dot{a}_{vk} = E_{v,k} \cdot a_{vk} + \mathcal{E} \cdot d_{vk,nm} \cdot e^{i\omega t} \cdot a_{nm}/2 + \mathcal{E} \cdot d_{vk,nm} \cdot e^{-i\omega t} \cdot a_{nm}/2 \quad (14)$$

Transition to quasienergy representation

$$a_{vk} = \sum_1 A_{vk,1} \cdot e^{i1\omega t} \quad (15)$$

yields

$$i\hbar A_{vk,1} = (E_{v,k} - 1 \cdot \hbar \cdot \omega) A_{vk,1} + \mathcal{E} \cdot d_{vk,nm} (A_{nm,1-1} + A_{nm,1+1})/2 \quad (16)$$

Eigenvalues of equations (16) in the case of constant light field ($\mathcal{E} = \text{const}$) are determined by

$$\lambda \cdot A_{vk,1}^\lambda = (E_{v,k} - 1 \cdot \hbar \cdot \omega) A_{vk,1}^\lambda + \mathcal{E} d_{vk,nm} (A_{nm,1-1}^\lambda + A_{nm,1+1}^\lambda)/2 \quad (17)$$

Where λ is quasienergy defined within the interval $-\hbar \cdot \omega/2 \leq \lambda \leq \hbar \cdot \omega/2$. General solution of (14) can be written as

$$\psi = C_\lambda \cdot A_{vk,1}^\lambda \cdot e^{i\lambda\omega t} \cdot e^{-i\lambda t/\hbar} \cdot |v, k\rangle \quad (18)$$

where summation is over the repeated indexes. Coefficients C_λ determine the behavior of the quantum system. In the case, when $\mathcal{E} = 0$ if $t < 0$ and $\mathcal{E} = \text{const} \neq 0$ if $t > 0$, coefficients C_λ are determined by relations

$$a_{vk}(t=0) \sum_\lambda C_\lambda \sum_1 A_{vk,1}^\lambda \quad (19)$$

The values $B_{vk}^\lambda = \sum_1 A_{vk,1}^\lambda$ are the elements of unitary matrix:

$$\sum_\lambda B_{nk}^\lambda \cdot B_{mj}^\lambda = \delta_{nk,mj}, \quad \sum_{nk} B_{nk}^\lambda \cdot B_{nk}^{\lambda'} = \delta_{\lambda,\lambda'} \quad (20)$$

It follows for C_λ that

$$C_\lambda = \sum_{vk} B_{vk}^\lambda \cdot a_{vk}(t=0) \quad (21)$$

The solution of above equations can be found explicitly if there is an exact resonance of exciting field with one of the transitions in the quantum system. Let a molecule is in the ground vibrational state with energy $E_{o,p}$ (sublevel p) and light field is in resonance with n-photon transition

$$E_{n,k} - E_{o,p} = n \cdot \hbar \cdot \omega + \Delta_{nk} \quad (22)$$

where Δ_{nk} is a small detuning. The solution of above equations can be found by means of perturbation theory technique. Compound matrix element V_n of n-photon transition is determined by n order of perturbation theory as

$$V_n = \left(\frac{\mathcal{E}}{2}\right)^n \cdot \sum_{m,i} \prod_{v=1}^n \frac{d_{vm,(v-1)i}}{\Delta_{(v-1)i} - \Delta_{vm}} \quad (23)$$

where summation is over all available intermediate levels, $d_{vm,(v-1)i}$ is dipole moment matrix element of transition $E_{(v-1),i} \rightarrow E_{v,m}$; detunings $\Delta_{v,m}$ are calculated in accordance with relation (22), by definition it is considered that in formula (23) $\Delta_{o,p} - \Delta_{1,i} = 1$.

Second order of perturbation theory determines the dynamic Stark shift of levels

that results in changes in the detunings. As a result the detuning of resonance of level $E_{n,k}$ is found to be

$$\Delta = \Delta_{nk} + \sum_m \frac{(\mathcal{E} \cdot d_{nk, (n-1)m}/2)^2}{E_{nk} - E_{(n-1),m} - \hbar\omega} - \sum_m \frac{(\mathcal{E} \cdot d_{nk, (n+1)m}/2)^2}{E_{(n+1),m} - E_{nk} - \hbar\omega} + \sum_m \frac{(\mathcal{E} \cdot d_{op, 1m}/2)^2}{E_{1,m} - E_{op} - \hbar\omega} \quad (24)$$

Summation must be done over all sublevels of the $v = 1$, $n = 1$, $n + 1$ states.

Only two quasienergy states or so called "dressed" states should be taken in account to compute the behavior of a system if there is only one resonance. In this case it is very simple to calculate the values of $A_{vk,l}^\lambda$ and C_λ , then the value of any physical operator \hat{P} can be calculated by formula

$$\langle P \rangle = C_\lambda \cdot A_{v'k',l'}^{\lambda'} \cdot P_{v'k',vk} \cdot C_\lambda \cdot A_{vk,l}^\lambda \cdot e^{i(\lambda' - \lambda + l'\omega - l\omega)t} \quad (25)$$

The mean population of upper level of n -photon resonance can be calculated explicitly:

$$N_{nk} = \frac{N_0}{2 \cdot [1 + (\Delta/V_n^2)]} \quad (26)$$

where N_0 is total population of resonant levels.

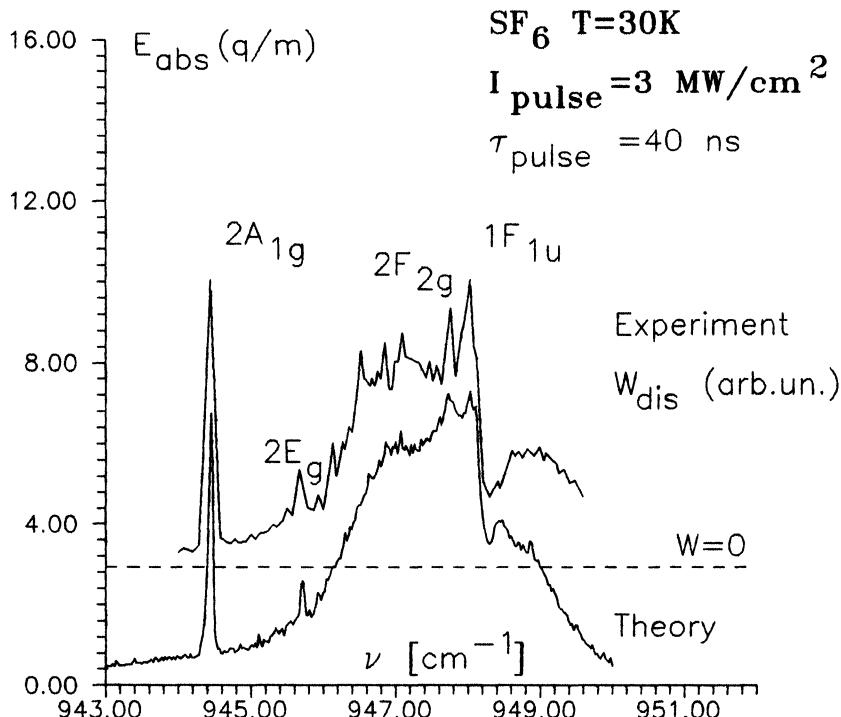


Figure 13 Calculated spectrum of absorbed energy and measured spectrum of dissociation of SF_6 .

The program package included the program calculating all possible one and two photon resonances at given laser frequency, matrix elements of dipole moment of v_3 mode and population of upper level by formula (26). The subsequent excitation of molecules in the region upper than $v = 2$ was calculated in the frame of rate equations. This approach differs from those used in Reference 28. We described excitation of $v \geq 3$ states with the help of rate equations and this simplification made it possible to utilize explicit formula to calculate dipole moment matrix elements while in Reference 28 dipole moment matrix elements were substituted by square averaged over M-projection. The latter made it possible to check polarization effects in the course of multiphoton excitation.

The simplifications of calculations were necessary because of limited power of computer employed (PC AT 386). The employment of more powerful computer makes it possible to calculate directly the contribution of three, four and more photon transitions in the excitation of vibrational ladder. But the results of calculations demonstrate that at laser pulse intensities less than 1 MW/cm^2 this contribution cannot play a significant role.

The result of calculation with parameters (rotational temperature, pulse intensity, pulse duration, etc.) close to those in experiment is shown in Figure 13. Comparison with measured dissociation spectrum reveals a good agreement between experimental and calculated data. It points out that one and two photon transitions play the main

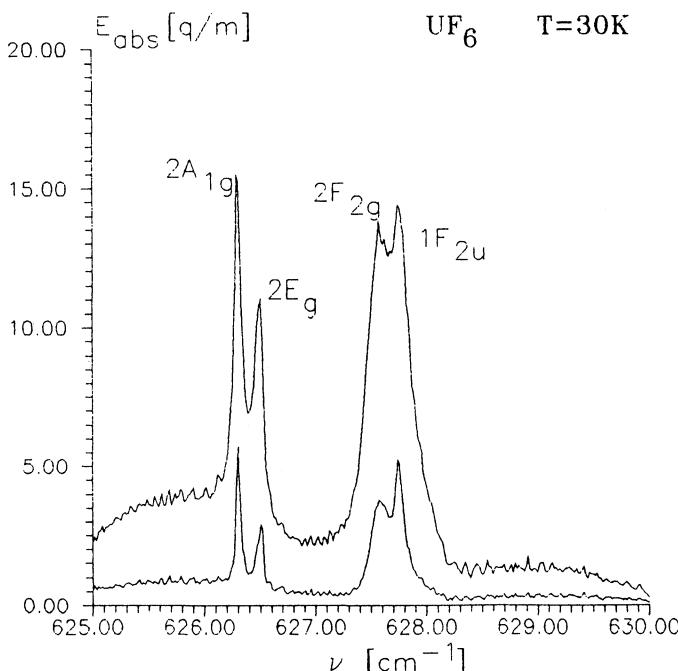


Figure 14 MPE spectra of UF_6 . Survey spectra calculated for laser pulse intensities $I = 3 \text{ MW/cm}^2$ (upper curve) and $I = 1 \text{ MW/cm}^2$ (lower curve). Laser pulse duration was taken to be 100 ns.

role in the excitation of a molecule and determine the spectral dependence of DL excitation process at intensity of laser field about 1 MW/cm^2 or less. The contribution of three, four and more photon transitions become significant if intensity is more than 1 MW/cm^2 . It should lead to smoothing of narrow peaks in spectral dependencies thus resulting in decreasing of selectivity of excitation. That is why it is multifrequency excitation that was used to decrease the intensity of laser field on the first stage of excitation with conserving of high efficiency of dissociation.

The program package was used to calculate MPE spectra of UF_6 that is of practical interest. The spectroscopic constants of UF_6 are known from linear spectroscopic measurements.^{29–31} The calculated MPE spectra are shown in Figure 14. The survey MPE spectra display the structure concerned with the two photon resonances. The peaks are narrow enough to reach an appreciable selectivity of excitation.

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