Transition Spectra in the Vibrational Quasicontinuum of Polyatomic Molecules. IR Multiple-Photon Absorption in SF_6. 1. Experimental Studies

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We studied in detail the IR multiple-photon (MP) absorption in the quasicontinuum of SF_6 molecule in the vicinity of the frequency of the mode ν_3. The molecules were preliminarily raised to the quasicontinuum by means of a pump laser pulse, and then we measured their IR MP absorption of a probe pulse, depending on its fluence and frequency ω_2, as well as on the initial excitation level (vibrational temperature) of the molecules. The latter was varied from room value to $T_{vib} = 1700$ K. The frequency ω_2 was varied in the range 884.18−944.2 cm^{-1}. The IR MP absorption spectra measured, as well as the fluence and T_{vib} dependences of MP absorption for various ω_2, are intended for making a comparison with the results of the theoretical modeling of the IR MP excitation dynamics and obtaining the spectral characteristics of the IR transitions of the SF_6 molecule in the quasicontinuum.

1. Introduction

The optical transition spectra of polyatomic molecules in the vibrational quasicontinuum (QC) have been the subject of much investigation (see reviews in refs 1−3). Apart from purely spectroscopic interest, these works have been largely initiated by the studies of intramolecular dynamics, as well as the possibility of the laser monitoring and control of chemical reactions (see, e.g., ref 3). One may single out two main lines of investigation into the spectral properties of the quasicontinuum. The first is the study of the *ground state → QC* transitions, and the second, the study of transitions *between* the states of the QC itself, i.e., the QC → QC transitions. A review of the works performed along the first line can be found in refs 4 and 5. For various reasons, primarily experimental difficulties, the QC → QC transitions have been studied much less. A review of the works available in the literature can be found in ref 6.

This work is a continuation of our research (see refs 6 and 7) aimed at studying the QC → QC transitions. The width and shape of transitions of this type are mainly governed by two factors: (1) the intramolecular vibrational relaxation of the mode of interest (the active mode ν_a), which leads to the *homogeneous broadening* of the spectrum and (2) the fact that the excited molecule possessing a certain energy of E_{vib} can be described by a vast set of combinations of the occupation numbers in various modes. The anharmonic transition frequency shift of any such combination being different from those of the other combinations, this leads to the statistical inhomogeneous broadening (SIB) of the spectrum (for details, see refs 6−9). The relative contribution of homogeneous and inhomogeneous broadening may be different for difference molecules. In the case of sufficiently *slow* IVR (for details, see ref 8), the main contribution to the shape of the vibrational transition band will come from the latter type of broadening, namely, the statistical inhomogeneous broadening. In our preceding work,[6] we suggested an approach making it possible to calculate the main profile parameters (the intensity, shape, and position of the band) of the QC → QC transitions in the case where the role of SIB is dominant. Using this approach, the above parameters were calculated for the modes ν_1 and ν_3 in SF_6. It turned out in particular that the statistical inhomogeneous broadening led to a Gaussian shape of the transition band profile in the quasicontinuum, distinct from the homogeneous broadening that yields a Lorentzian shape of the band profile. This approach was experimentally verified by Malinovsky et al.[7] who obtained good agreement between experimentally measured and theoretically calculated Raman spectra of the mode ν_1 in SF_6 over a wide range of vibrational temperatures ($T_{vib} = 850−1600$ K). These experiments allowed the authors to conclude that the SIB effect in SF_6 in fact made a decisive contribution to the width of the QC → QC transition band, but they failed to obtain any quantitative data as to the contribution from the homogeneous broadening.

The current status of the theory does not as yet allow calculating homogeneous broadening values for particular molecules. As a consequence, the possibility of experimental determination of this parameter is essential to both the development of the theory of optical spectra in the quasicontinuum and the study of the intramolecular dynamics of polyatomic molecules. Therefore, the chief objective of this work was to develop a suitable method and measure the homogeneous broadening parameters of the QC → QC transitions. We selected the SF_6 molecule to serve as the object of study. Insofar as the contribution from the statistical inhomogeneous broadening for this molecule is predominant, the homogeneous broadening can be regarded as some addition, and so its magnitude can be found from comparison between experimental spectra and theoretical spectra calculated in the SIB approximation. It was exactly this approach that was contemplated in ref 7 to be used to determine the homogeneous broadening for the Raman active mode ν_1 in SF_6. However, at the edge of the spectrum, where the Lorentzian wings must make the greatest contribution, the sensitivity and accuracy of measurement proved insufficient for the implementation of this approach. It should, however, be emphasized that in the case of spontaneous Raman spectra, all transitions between the states of the quasicontinuum are of single-quantum character. And placed at the root of this work was the idea that the

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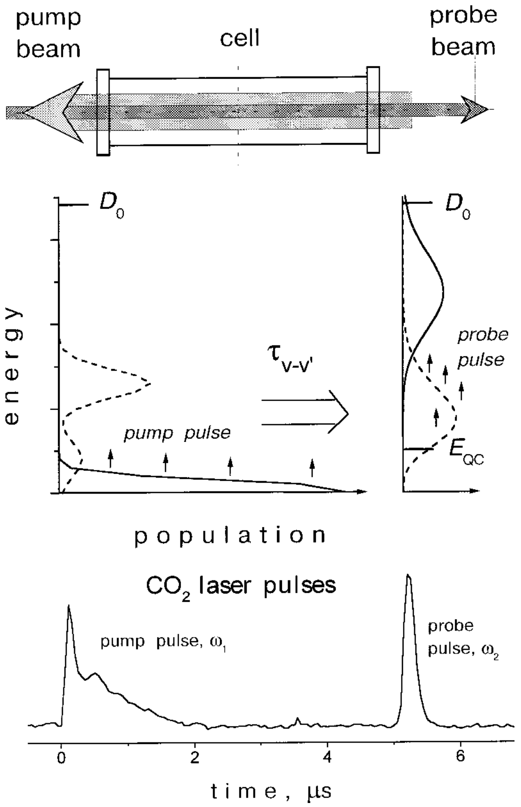

Figure 1. Illustrating the pump−probe technique for studying the IR MP absorption process in the quasicontinuum.

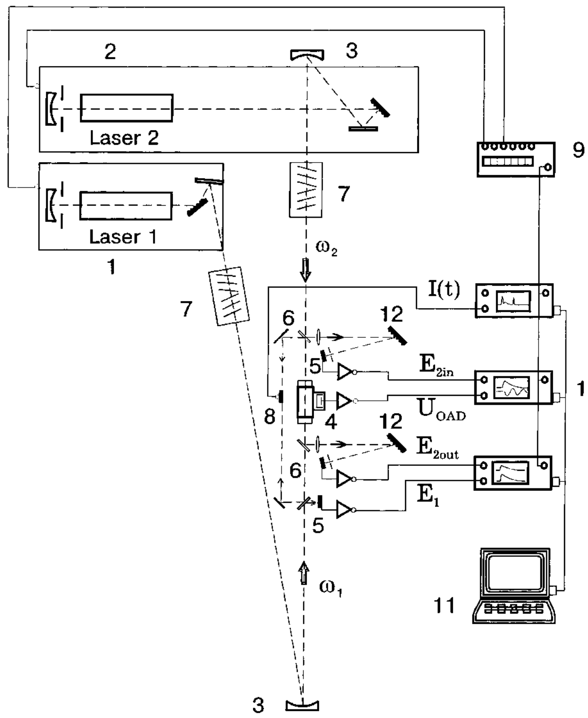

Figure 2. Schematic diagram of the experimental setup: 1, pump CO_2 laser; 2, probe CO_2 laser; 3, mirrors; 4, absorption cell with OAD; 5, pyroelectric calorimeters; 6, beam splitters; 7, CaF_2 plate attenuators; 8, photon-drag detector; 9, triggering system; 10, digital scopes; 11, PC; 12, diffraction gratings.

relatively small contribution from the Lorentzian wings could be "accumulated" in a sequence of a large number of IR transitions, which can be realized in the case of multiple-photon (MP) absorption. Therefore, comparing between experimentally measured MP absorption spectra and their theoretical counterparts calculated in the SIB approximation will make it possible to obtain information on the homogeneous broadening parameters.

The IR MP absorption process in SF_6 was studied in principle by many authors (see, e.g., reviews in refs 10 and 11). However, it proved impossible to use the experimental results already available in the literature for the implementation of the above approach: as will be evident from the text below, this calls for a high accuracy of measurement and the knowledge of all the measurement procedure details. For this reason, the present investigation necessitated taking detailed measurements of the IR MP absorption spectra of the SF_6 molecules preliminarily raised to the quasicontinuum over a wide range of frequencies in the vicinity of the mode ν_3.

The investigation results obtained are presented as follows. The first part (this paper) presents the results of experimental measurements of the IR MP absorption spectra of SF_6 in the quasicontinuum. The second part (the associated paper[12]) presents the results of the analysis of the above experimental data on the basis of the model developed of the IR MP excitation of the molecules in the quasicontinuum.

2. Experimental Section

The experimental study of the IR MP absorption process in SF_6 molecules in the quasicontinuum was conducted using the pump−probe technique (Figure 1). To minimize the contribution from absorption in the system of the lower "discrete" levels lying below the quasicontinuum boundary (for SF_6, $E_{QC} = 5000 \pm 500$ cm^{-1}),[13] the molecules under study were preliminarily raised to the quasicontinuum by means of a pump CO_2 laser pulse. Then, after the lapse of some delay time τ_d, a second, probe CO_2 laser pulse was passed through the excited medium, and its absorption was measured as a function of its fluence Φ_2 and frequency at various preliminary excitation levels of the molecules. The population distribution formed during the passage of the pump pulse may be of nonequilibrium character (see, e.g., refs 13 and 14), and so the delay time τ_d was chosen so that the vibrational distribution established as the result of the V−V′ relaxation of the molecules between the pulses was known to be of *equilibrium* character. This procedure was specially introduced in order that in the subsequent modeling of IR MP excitation within the quasicontinuum region in ref 12 we can deal with a well-defined initial vibrational distribution function, namely, a Boltzmann distribution.

The experimental setup used is shown schematically in Figure 2. It basically consists of two CO_2 lasers, a pump and a probe laser, an absorption cell, a system for monitoring and controlling the laser beam parameters, and also electronic equipment necessary to detect and process the experimental data.

The shapes of the pump and probe laser pulses are shown in Figure 1. The total (full-width) pump pulse duration did not exceed 2 μs, and the probe pulse duration lasted for some 200 ns (fwhm) and had practically no "tail". To extend the tuning range of the probe CO_2 laser, a provision was made for the possibility of its operation on a gas mixture containing $^{13}CO_2$. After passing through the focusing system 3, the pump and probe laser beams (both in the TEM_{00} mode) passed through the absorption cell 4 containing SF_6 contrary to each other, the probe beam being "nested" in the pump one. The energy of each beam was measured at the entrance and exit of the absorption cell with the aid of pyroelectric calorimeters. The gratings 12 served to optically isolate the pump and probe beams. The absorption cell 4 was equipped with a microphone, which made possible the optoacoustic measurement of the power absorbed. The

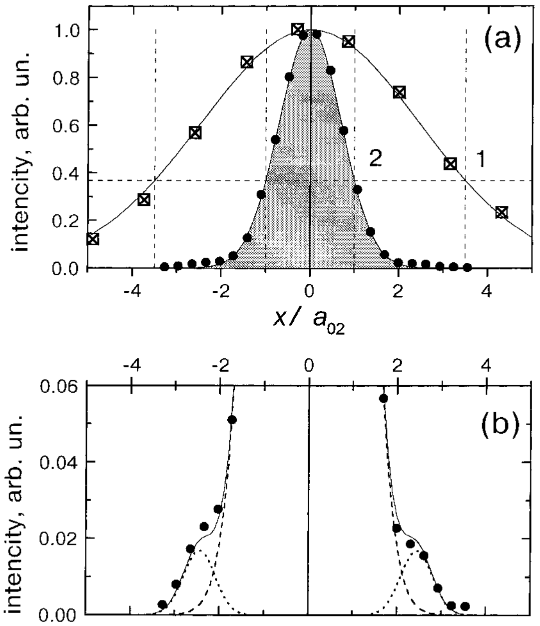

Figure 3. (a) Radial fluence distribution in the laser beams: 1, pump beam; 2, probe beam; dots, experimental data points; curves, Gaussian fitting with $a_{01} = 2.8$ mm and $a_{02} = 0.8$ mm. (b) Fluence distribution at the base of the probe beam: dots, experimental data points; solid curve, fitting by eq 2 in the text; dashed curves, contribution of different parts of eq 2.

signals from the detectors were digitized and fed to a personal computer to be integrated and processed.

The preliminary analysis of the experimental data revealed the need to know as precisely as possible the spatial radiation distribution in the pump, and especially so in the probe beam, and therefore these characteristics were thoroughly checked in each series of experiments. Figure 3a shows the radial intensity distribution in the pump and probe beams, measured in the center of the absorption cell by means of a pinhole 50 μm in diameter. It can be seen that the radiation intensity distribution in both beams is well described by the Gaussian function

$$\Phi_i = \Phi_{0i} \exp(-r^2/a_{0i}^2) \qquad (1)$$

where the parameters a_{0i} are $a_{01} = 2.8$ mm and $a_{02} = 0.8$ mm for the pump and probe beams, respectively. The effective beam cross-sectional area in this work was taken to be $S_i = 2\pi a_{0i}^2$, i.e., the area through which passes 86% of the energy E_i of the pump ($i = 1$) and probe ($i = 2$) beams. Accordingly, the effective fluence characteristic is $\Phi_i = E_i/S_i$. The ratio chosen between the cross-sectional dimensions of the pump and probe beams ($a_{01}/a_{02} = 3.5$, $S_1/S_2 = 12.25$) was the result of a tradeoff of the energy output of the CO_2 lasers used and the fluence required against the need to provide for the maximum uniformity of the laser beams over the length of the absorption cell (the fluence Φ_{02} varied by no more than 2% over the cell length $L = 10$ cm). It can be seen from Figure 3a that with the ratio a_{01}/a_{02} being as it is, the probe beam passes in the region where the pump beam intensity and hence the vibrational temperature of the preexcited molecules vary quite perceptibly in the radial direction. Therefore, this nonuniformity was allowed for in the subsequent theoretical interpretation of the measurements taken (see ref 12). The more detailed probe beam profile measurements showed (Figure 3b) that at the edge of the spatial distribution there was an additional "ring" associated with the diffraction of radiation by the intracavity diaphragm (Figure 2). The radiation intensity in this ring was no more than 2% of the magnitude of Φ_{02}, and the energy contained therein amounted to some 7% of the total probe pulse energy. Finally, when the experimental measurement results were interpreted, use was made of the following expression for the intensity distribution in the probe beam:

$$\Phi_2(\xi) = \Phi_{02}[\exp(-\xi^2) + 0.017 \exp(-(|\xi| - 2.45)/0.5)^2] \qquad (2)$$

where $\xi = x/a_{02}$.

The SF_6 molecules were preexcited into the quasicontinuum by the pump pulse on the 10P(16) CO_2 laser line ($\omega_1 = 947.74$ cm^{-1}). The pressure of the SF_6 gas in the absorption cell was $p = 1$ Torr and the delay time between the pump and probe pulses was $\tau_d = 5$ μs, which made the parameter $p\tau_d$ equal to 5 μs·Torr. According to ref 15, with the level of excitation of the molecules to the quasicontinuum being similar to that in the present work, the "complete" establishment of vibrational equilibrium in SF_6 as a result of the V−V′ relaxation process already occurs at $p\tau_d = 3.6$ μs·Torr. Therefore, with the parameter $p\tau_d$ selected at 5 μs·Torr, it can be taken that the vibrational distribution established by the instant the probe pulse arrived is known to be an equilibrium Boltzmann distribution; at the same time, the diffusion of the molecules out of the excitation region can be disregarded, and the contribution from the V−T/R relaxation processes can be considered to be small ($p\tau_{VT} = 122$ μs·Torr[16]).

The quantities subject to measurement in this work were the average numbers N_1 and N_2 of quanta absorbed per molecule from the pump and probe beams, respectively:

$$N_i = \Delta E_i/(\hbar\omega_i S_i N_0 L) \qquad (3)$$

where N_0 is the density of the molecules, ΔE_i is the energy absorbed over the length L of the absorption cell, $\hbar\omega_i$ is the quantum energy, and S_i is the beam cross-sectional area. The number N_1 is a function of Φ_1 alone, i.e., $N_1 = N_1(\Phi_1)$, whereas N_2 is a function of several parameters: $N_2 = N_2(\omega_2, \Phi_2, T_{vib})$, where $T_{vib} = T_{vib}(\Phi_1)$ is the vibrational temperature of the preexcited SF_6 molecules.

In IR MP excitation experiments, the absorbed energy is usually determined either by the direct calorimetric measurement of the laser pulse energy at the entrance and exit of the absorption cell or by means of the optoacoustic (OA) technique.[10] The latter technique is especially convenient to apply in the case of sufficiently high fluence values, $\Phi \approx 1$ J/cm^2, and an optically thin absorbing layer. As noted earlier, the absorption cell used by us allowed for measuring OA signals. But it turned out that this technique could not provide the accuracy necessary in our investigation to measure the magnitude of the energy absorbed. It was found that the coefficient of coupling between the energy absorbed and the magnitude of the OA signal depended on the probe pulse frequency ω_2. The analysis of the causes of this dependence (for details, see ref 17) showed that it was due to the dependence of the V−T/R relaxation rate constant on the vibrational excitation level of the SF_6 molecules and the form of the vibrational distribution of these molecules. It turned out (see ref 12) that the form of this distribution for SF_6 strongly depended on the probe pulse frequency ω_2, even with the number N_2 being the same. For these reasons, the experimental data presented below were obtained by the direct calorimetry method. Note that no more than 30−40% of the probe pulse energy was in most cases absorbed in the absorption cell under our experimental conditions, but nevertheless, this Φ_2 variation over the absorption

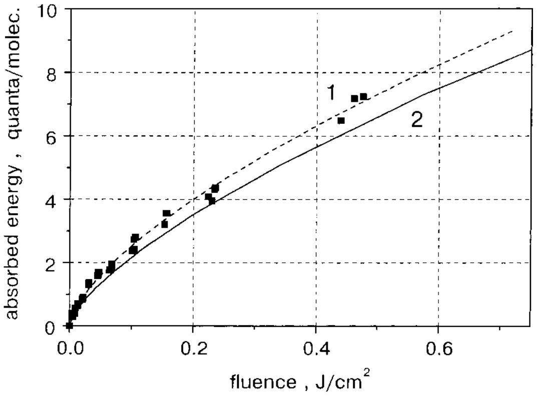

Figure 4. Average energy (quanta per molecule) absorbed from the pump pulse as a function of its fluence: 1, experimental curve $N_1(\Phi_1) = \Delta E_{abs}/(\hbar\omega_1 N_0 L S_1)$ (see text); 2, local average number n_1 of absorbed quanta, obtained by deconvolution from curve 1. $p_{SF_6} = 1$ Torr; 10P(16) CO_2 laser line.

cell length was taken into consideration in the subsequent interpretation[12] of the measurement results obtained.

3. Results and Discussion

To study the IR MP absorption process in the quasicontinuum with the pump–probe experimental scheme (Figure 1), it is necessary to know the initial average energy (vibrational temperature) of the preexcited SF_6 molecules. To this end, we took IR MP absorption measurements for the pump laser beam. Figure 4 presents the average number N_1 of quanta absorbed from the pump beam as a function of its fluence Φ_1. Recall that the quantity N_1 by definition (see (3)) characterizes MP absorption for a highly nonuniform (in the radial direction) laser beam. At the same time, to interpret the measurement results, it is necessary to know the *local* average number n_1 of absorbed quanta for the given fluence Φ (there only remains averaging over the vibrational distribution function). This quantity can be found by deconvolving the experimental curve. For Gaussian beams, the deconvolution procedure reduces to taking the logarithmic derivative.[18] In our case, $n_1(\Phi)$ is given by

$$n_1(\Phi) = 2N_1(\Phi_1)\frac{\mathrm{d}\ln N(\Phi_1)}{\mathrm{d}\ln \Phi_1} \tag{4}$$

(Note, in eq 4 numerically $\Phi = 2\Phi_1$.) The result of such a deconvolution is shown by curve *2* in Figure 4. It was precisely these $n_1(\Phi)$ values that were later used to characterize the preexcitation level of the molecules and also to calculate (by the Planck quantum heat capacity formula) the local values of the vibrational temperature $T_{vib} = T_{vib}(r)$ in the theoretical interpretation of the results. Note that as n_1 varies from 4 to 14 quanta per molecule, the vibrational temperature of SF_6 molecules varies (with due regard for the initial energy store at $T = 293$ K) approximately from 770 to 1730 K. It should also be noted that with n_1 varying over the above range, the variation of T_{vib} on the axis of the beam over the length of the absorption cell was no more than 2%, and so it was neglected in the subsequent discussion.

The IR MP absorption measurements for SF_6 molecules preliminarily raised to the quasicontinuum were taken at 10 different values of the probe pulse frequency in the range from 884.18 to 944.2 cm^{-1} containing intense $^{12}CO_2$ and $^{13}CO_2$ laser lines. The values obtained for the average number N_2 of absorbed quanta as a function of n_1 and Φ_2 ($N_2 = N_2(n_1,\Phi_2)$) are presented in Figure 5 for three ω_2 values (884.18, 903.75, and 936.8 cm^{-1}). These frequency values correspond to the "red", approximately central, and "blue" regions of the IR MP absorption spectrum (see below). As one can see from this figure, there in fact occurs multiple-photon absorption: the number N_2 reaches as high a value as 20 quanta per molecule. One can also see that the character of IR MP absorption, i.e., the relationship between N_2 on one hand and n_1 and Φ_2 on the

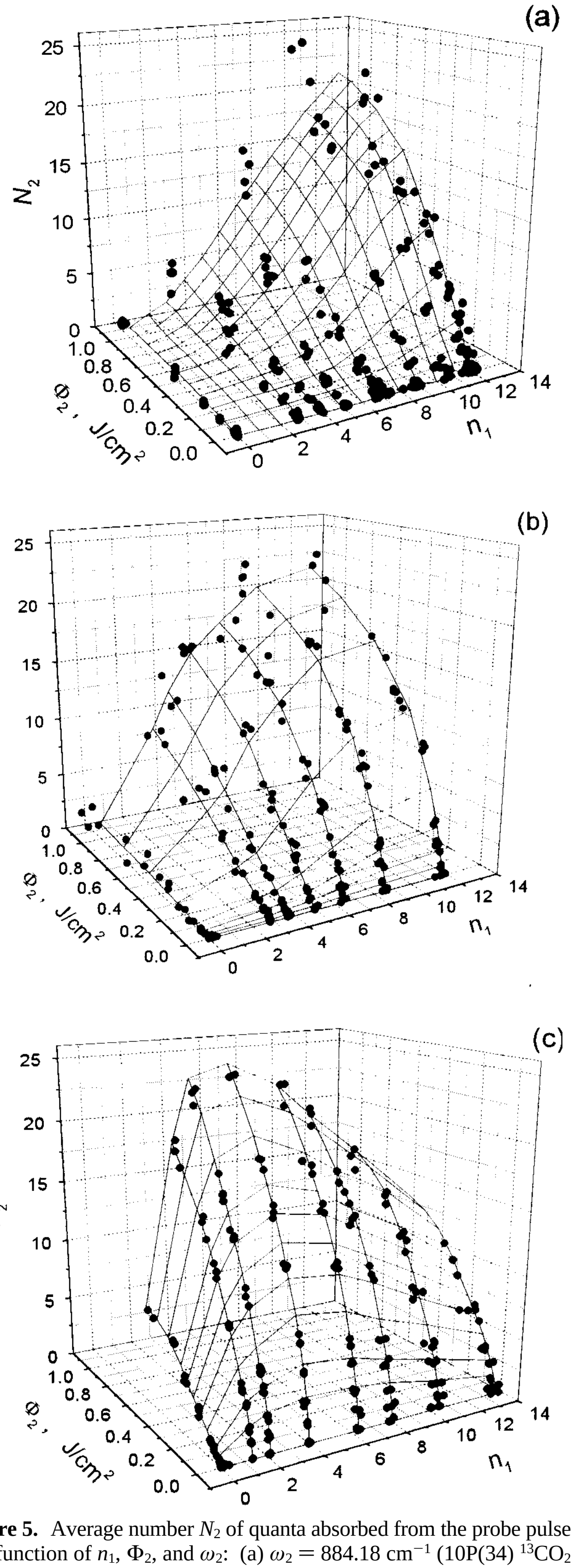

Figure 5. Average number N_2 of quanta absorbed from the probe pulse as a function of n_1, Φ_2, and ω_2: (a) $\omega_2 = 884.18$ cm^{-1} (10P(34) $^{13}CO_2$ laser line); (b) $\omega_2 = 903.75$ cm^{-1} (10P(12) $^{13}CO_2$ laser line); (c) $\omega_2 = 936.8$ cm^{-1} (10P(28) $^{12}CO_2$ laser line).

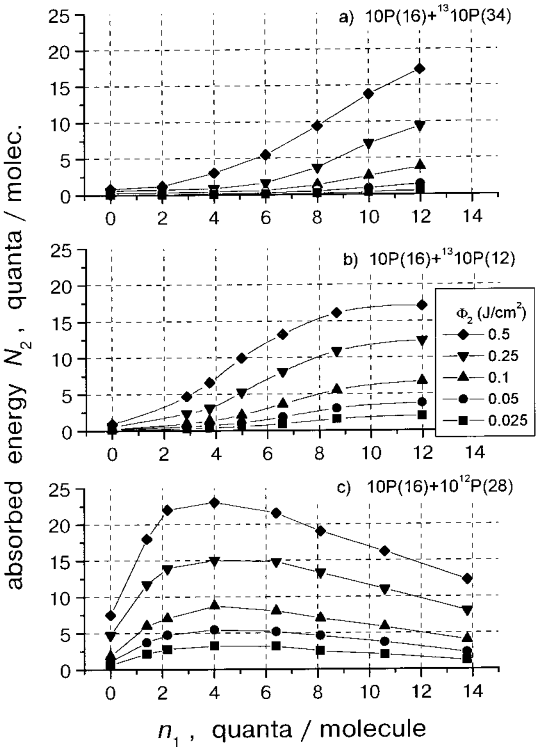

Figure 6. Average number N_2 of quanta absorbed from the probe pulse as a function of the number n_1 of quanta absorbed from the pump pulse for some values of the probe pulse fluence Φ_2: (a) $\omega_2 = 884.18$ cm^{-1}; (b) $\omega_2 = 903.75$ cm^{-1}; (c) $\omega_2 = 936.8$ cm^{-1}.

other, depends materially on the radiation frequency ω_2: the two-dimensional surfaces $N_2 = N_2(n_1,\Phi_2)$ differ perceptibly between different regions of the MP spectrum. These differences are well illustrated by Figure 6 presenting the functions $N_2(n_1)$ for various values of the probe pulse fluence Φ_2 for three characteristic ω_2 values. (The curves of Figure 6 were obtained by passing sections through the surfaces $N_2 = N_2(n_1,\Phi_2)$ in Figure 5 for the selected fixed values of Φ_2.) As can be seen from Figure 6, the character of the function $N_2(n_1)$ differs substantially between the ω_2 values selected. At the "blue" end of the MP absorption spectrum ($\omega_2 = 936.8$ cm^{-1}) there is observed from the very beginning the rise of N_2 with increasing n_1, which reaches its maximum and then drops. For $\omega_2 = 903.75$ cm^{-1}, a noticeable absorption of the probe pulse energy starts with $n_1 \approx 1.5$ quanta per molecule; it grows higher with increasing n_1 and then tends to saturation. At the "red" end of the spectrum ($\omega_2 = 884.18$ cm^{-1}) the absorption of the probe pulse energy becomes noticeable only at a comparatively high preexcitation level of the molecules, $n_1 \geq 5$ quanta per molecule. Thereafter N_2 increases monotonically with increasing n_1.

This difference in the behavior of the function $N_2(n_1)$ between different regions of the IR MP absorption spectrum is sufficiently easy to explain qualitatively. The anharmonicity of vibrations causes the frequency of transitions in the vicinity of the mode being excited (the mode ν_3 of SF_6 in the given case) to shift toward the red side as the vibrational energy of the molecule grows higher. At the "blue" end of the IR MP absorption spectrum (specifically at $\omega_2 = 936.8$ cm^{-1}) in good interaction with radiation are those molecules whose preexcitation level is relatively low, $n_1 < 4$. As their preexcitation level is raised, the molecules drop off resonance with radiation, and MP absorption starts decreasing. The situation at the "red" end is quite the opposite: when n_1 is low, it is only high-energy molecules lying at the far edge of the vibrational distribution that can interact with radiation, and so MP absorption is weak. As n_1 grows higher, the number of molecules interacting with radiation increases, and MP absorption increases accordingly.

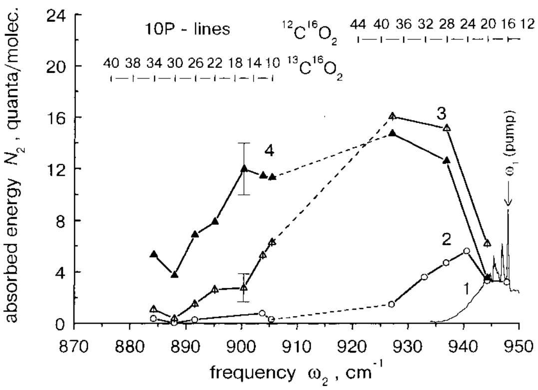

Figure 7. IR MP absorption spectra $N_2(\omega_2,n_1,\Phi_2)$ for some fixed n_1 values (in quanta per molecule) at $\Phi_2 = 0.25$ J/cm^2: 1, linear absorption spectrum of SF_6; 2, $n_1 = 0$; 3, $n_1 = 5$; 4, $n_1 = 9$.

This qualitative reasoning agrees with the form of the IR MP absorption spectra measured. Figure 7 presents as an example the IR MP absorption spectra for two preexcitation level values, $n_1 = 5$ and $n_1 = 9$ quanta per molecule, at which most of the molecules are already in the quasicontinuum. The probe pulse fluence Φ_2 in that case amounts to 0.25 J/cm^2. The same figure presents for comparison another two spectra: the IR MP absorption spectrum in the absence of preexcitation ($n_1 = 0$, $\Phi_1 = 0$) and the spectrum of linear-IR absorption at room temperature. It can be seen that the preexcitation of the molecules to the quasicontinuum leads to a dramatic transformation of the IR MP absorption spectrum: it broadens materially and shifts toward the "red" side (cf. curves 2−4). The width of the spectrum reaches some 50 cm^{-1} (curve 4). Unfortunately, it proved impossible to exactly determine the position of the maximum of these spectra (curves 3 and 4) because of the limited tuning range of the $^{12}CO_2$ and $^{13}CO_2$ lasers. Note also that in accordance with what has been said above, increasing n_1 reduces MP absorption in the "blue" region of the spectrum and increases it in the "red" region (cf. curves 3 and 4).

In this work, we will restrict ourselves to the above simple qualitative explanation of the results obtained. Their detailed interpretation on the basis of the theoretical modeling of the IR MP excitation dynamics of SF_6 molecules in the quasicontinuum is presented in our companion paper.[12]

4. Conclusion

Using the pump−probe technique, we experimentally studied the IR MP absorption process in SF_6 molecules in the quasicontinuum in the vicinity of the ν_3 mode frequency of this molecule, with special emphasis being on the accuracy of measurement and detailed knowledge of all experimental conditions. We measured MP absorption in SF_6 in the quasicontinuum as a function of the IR laser radiation fluence and frequency and the preexcitation level (vibrational temperature) of the molecules in the quasicontinuum. The initial vibrational temperature of the molecules was varied from room value to $T_{vib} = 1700$ K, and the probe radiation frequency, in the range from 944.2 to 884.18 cm^{-1}.

It turned out that the preliminary excitation of the molecules to the quasicontinuum drastically affected the IR MP absorption spectrum, broadening it substantially and shifting it toward the long-wavelength side as compared with the spectra measured at room temperature. The experimental data set obtained enabled us to obtain both IR MP absorption spectra over a wide range of excitation conditions and the relationships between IR MP absorption on one hand and the probe radiation fluence and the vibrational temperature T_{vib} of the molecules on the other, necessary for the subsequent theoretical modeling of the IR MP excitation dynamics and finding of the spectral characteristics of IR transitions of the SF_6 molecule in the quasicontinuum.

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