J. Phys. Chem. A **1998,** *102,* 9353−9359

Transition Spectra in the Vibrational Quasicontinuum of Polyatomic Molecules: Raman Spectra of Highly Excited SF_6 Molecules

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Received: February 20, 1998; In Final Form: June 8, 1998

The detailed studies of spontaneous Raman spectra are performed for highly excited SF_6 molecules in the vicinity of the ν_1 mode. Interpretation of the measured spectra is given within the framework of theoretical model, which assumes the dominating role of the *statistical inhomogeneous broadening* in the spectrum formation. A good agreement is achieved between the experimental and theoretical spectra throughout the whole temperature range used ($T_{vib} = 850-1660$ K). A conclusion is drawn that the *homogeneous broadening* due to intramolecular vibrational relaxation gives a relatively small contribution to the observed spectra.

1. Introduction

The spectra of vibrational transitions of highly excited molecules in the region of what is known as the vibrational quasicontinuum (QC) was the subject of a large number of works (see, e.g., refs 1−3 for references). Such a great interest in this problem is largely due to the studies into intramolecular dynamics, including the possibility of laser control of the dynamics of chemical reactions (see, e.g., ref 3 for a recent review). It should be noted that by virtue of a number of reasons, most investigations on the spectroscopy of the QC deal with the *ground state* → *QC* transitions. A review of these works can be found in ref 4; see also ref 5. The transitions between the states of the quasicontinuum proper (*QC* → *QC* transitions) have proved more difficult to study experimentally. At the same time, in a number of cases it is this type of transition that is of interest. As an example, one may cite the process of IR multiple photon excitation of molecules.

As a rule, the spectra of vibrational transitions in the QC are studied using the pump−probe technique. The molecules of interest are first excited vibrationally and then studied by various methods. Specifically, these include linear IR spectroscopy,[6,7] spontaneous Raman scattering spectroscopy,[8,9] IR fluorescence spectroscopy,[10,11] and coherent anti-Stokes Raman spectroscopy (CARS).[12,13] One of the problems arising in the study of QC−QC transitions is associated with the difficulties involved in the preparation of a sufficiently large number of molecules in a narrow energy interval in the QC. This problem was in great part overcome in refs 14 and 15. In the former work, it was suggested that, to prepare highly excited molecules, use should be made of the inverse electronic relaxation effect.[16] The authors of the latter work developed the photodissociative IR spectroscopy technique, which enabled them to measure the spectra of IR absorption from states above the dissociation limit of such molecules as CF_3I,[15] $(CF_3)_3CI$,[17] and C_2F_5I, C_3F_7I, and n-C_4F_9I.[18]

The existing data show that the shape and width of the QC−QC transition spectra are governed by two factors: (1) intramolecular vibrational relaxation (IVR) from the mode ν_a of interest, which leads to the *homogeneous broadening* of the spectrum, and (2) the fact that the vibrational energy of the molecule near some E_{vib} values can be represented by a great number of different sets of occupation numbers in various modes, which leads to the *inhomogeneous broadening* of the spectrum. Origin of the latter type of broadening[19] is that it would exist if there are no IVR at all, but a large *ensemble* of the *regular* states at E_{vib}, i.e., those that can be described in terms of the mode occupation numbers, is under observation. Let us assume now that IVR takes place but is relatively *slow*. Then, the inhomogeneous spectrum cannot be significantly perturbed (see ref 19 for the rigorous criterion of this *slowness*, which is, roughly, smallness of the IVR rates with respect to the inhomogeneous width). In practice, direct measurement and/or theoretical evaluation of IVR rates are hard points of interpretation of QC−QC spectra. So, a natural procedure of interpretation of any QC−QC spectrum would start from calculation of the inhomogeneous broadening. Fortunately, those calculations require only ordinary spectroscopic parameters, fundamental mode frequencies, and anharmonicity constants, which can be obtained from spectroscopy of low vibrational states. Some analytical estimates of the magnitude of inhomogeneous broadening were made in refs 19 and 20. In our recent work,[21] we have developed an approach allowing, in our view, for sufficiently reliable calculation of the intensity, shape, and position of IR transition bands where this type of broadening is predominant, which is more precise than the previous analytical estimates. To emphasize the statistical, fluctuation character of this type of broadening, we use the name *statistical inhomogeneous broadening* (SIB). In general, dominance of SIB can be approved only by comparison between the theory and the experiment. The same may be said about dominance of the homogeneous broadening as well. Really, there is evidence that each type of broadening can be dominant, depending on the molecule in hand (see references in ref 21). Using the above approach, we have calculated[21] the parameters of the inhomogeneous QC−QC transition spectra for the modes ν_3 and ν_1 of the SF_6 molecule and for the mode ν_3 of the WF_6 molecule. It has been found that the calculated spectra are rather wide to believe that the principal contribution to the width of QC−QC transitions comes from the SIB effect. To illustrate, according to the calculations of ref 21, the inhomogeneous width of transitions in the vicinity of the frequency of the ν_3 mode of

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10.1021/jp981232b CCC: $15.00

SF_6 varies from about 10 cm^{-1} to about 34 cm^{-1} as E_{vib} varies between 7000 and 30 000 cm^{-1}. At the same time, according to ref 20, the *homogeneous* width within the same interval of E_{vib} values ranges between $\approx$1 and $\approx$6 cm^{-1}. So great a difference between the inhomogeneous and homogeneous broadening values gives grounds for comparison between experimental and theoretical spectra when the latter considers the contribution from the SIB only. In this work, we present the results of such comparison for the mode ν_1 of SF_6.

In our experiment, the molecule was heated to various vibrational temperatures by way of the IR multiple photon excitation (IR MPE). The spectrum of spontaneous Raman scattering was then measured near the frequency of the ν_1 mode in conditions of equilibrium vibrational distribution. The Raman spectra thus obtained were compared with their theoretical counterparts calculated on the basis of the model suggested in ref 21. It should be noted that our choice of the Raman scattering technique for this work has largely been due to the fact that there is only one narrow Q-branch in the Raman spectrum of the ν_1 mode of the SF_6 molecule, which minimizes the contribution from its rotational structure to the resultant spectrum. This is quite different, for example, from IR transitions in the ν_3 mode where one should take account of the wide $P-Q-R$ structure present.[10]

The results obtained are presented below.

2. Experiment

2.1. Measurement Technique. The Raman scattering pump$-$probe technique used in the present work has been described in sufficient detail in refs 9 and 22. Let us recall some information about it. At the root of the technique is the simple relationship between the scattered radiation intensity and the population of the vibrational mode υ_i being probed. The cross section of a Raman transition from the state with the occupation number n_i in this mode is

$$\sigma_{n_i,n_i+1} = \sigma_{0,1}(n_i + 1) \qquad \sigma_{n_i,n_i-1} = \sigma_{0,1} n_i \qquad (1)$$

for the Stokes and anti-Stokes transitions, respectively. Equation 1 leads in particular to a simple linear relationship between the integral (over the levels of the mode being probed) intensity of the anti-Stokes signal I^{aS} and the average occupation number $\langle n_i \rangle$ or the average vibrational energy $\langle \epsilon_i \rangle$ in this mode:

$$I_i^{\text{aS}} = A_i^{\text{aS}} \langle n_i \rangle = A_i^{\text{aS}} \langle \epsilon_i \rangle / h\nu_i \qquad (2)$$

The constant A_i can easily be found (see below). Thus, eq 2 allows one to measure the *absolute* value of the vibrational energy in the mode being probed.

The measurement scheme is presented in Figure 1. The IR MP excitation of the molecules of interest was effected by a TEA CO_2 laser ($\tau_{\text{pump}} = 15-25$ ns) whose radiation was focused by means of a cylindrical lens into the cell containing the gas under study (not shown in the figure). A second harmonic pulse from a Nd:YAG laser ($\tau_{\text{probe}} = 7$ ns) was used for probing purposes and it traversed the excited gas region after some delay of τ_{d}.

The scattered radiation was collected by means of a suitable optical system and then focused onto the entrance slit of a triple polychromator. After passing through this optical instrument, the signal was registered by means of a gated optical multichannel spectroanalyzer. The system provided for a spectral resolution of up to 1 cm^{-1} in the green region of the spectrum. All spectral measurements were taken in a photon counting mode. In these experiments, the characteristic signal accumulation time amounted to 1$-$2 h for a single spectrum (at a pulse repetition rate of 6.25 Hz). The IR MP excitation of the SF_6 molecules was effected via the strongest IR mode υ_3. The molecules were excited on the 10P(24), 10P(16), and 10P(12) CO_2 laser lines at various values of the energy fluence Φ. The initial gas temperature in the cell was equal to -47 °C. The gas pressure p amounted to 0.6 Torr, which provided for collisionless IR MP excitation conditions at the IR pulse duration used.

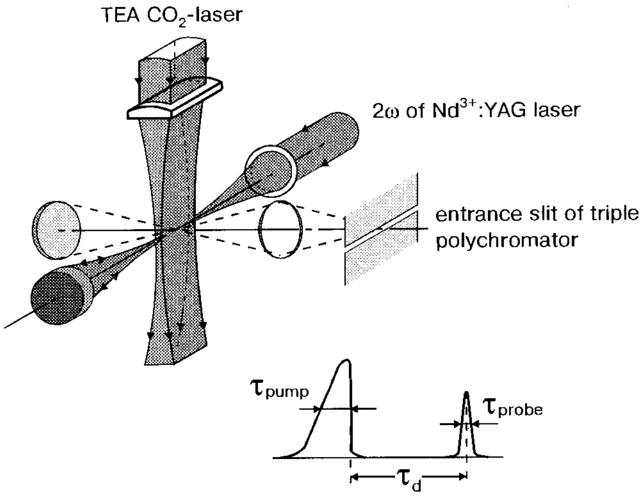

Figure 1. Experimental scheme.

To compare between theoretical and experimental spectra, one should know the vibrational temperature T_{vib} of the molecules in the latter case, and to determine this temperature, use was made of eq 2 (for more details, see ref 22). The value of the constant A_i can be found from the spectrum-integrated anti-Stokes signal I^{aS} measured for a *known* gas temperature, the average number of quanta in the mode, $\langle n_i \rangle$, entering into relation (2) being calculated by Planck's formula for quantum heat capacity. With the constant A_i thus found, one can determine in a similar way the average number of quanta in the mode being probed following the IR MP excitation of the molecules, and then the vibration temperature T_{vib} as well, provided that the vibrational distribution is of equilibrium character (see below).

2.2. Measurement Results. As noted in the Introduction, we selected for measurement purposes the Raman-active mode υ_1 (774.54 cm^{-1}) of SF_6. In this work, we present the results of measuring "equilibrium" spectra in the vicinity of the frequency of this mode, obtained in conditions of equilibrium Boltzmann vibrational distribution attained after the passage of the exciting IR pulse. (The results of measuring "instantaneous"spectra will be presented in ref 23.) The choice of "equilibrium" spectra in the present work is due to the fact that to compare correctly between experimental and theoretical spectra, one should know as accurately as possible the distribution function of the level populations in vibrational energy. For the equilibrium distribution, it is known to be the Boltzmann function.

To obtain "equilibrium" spectra, their measurements were taken with a delay of τ_{d} between the pump and probe pulses, when the parameter $p\tau_{\text{d}}$ equaled 2.1 μs·Torr. According to ref 7, under such conditions, an equilibrium *vibrational* distribution with a vibrational temperature T_{vib} corresponding to the stored vibrational energy has enough time to set in as a result of the $V-V'$ relaxation process. At the same time, the translational

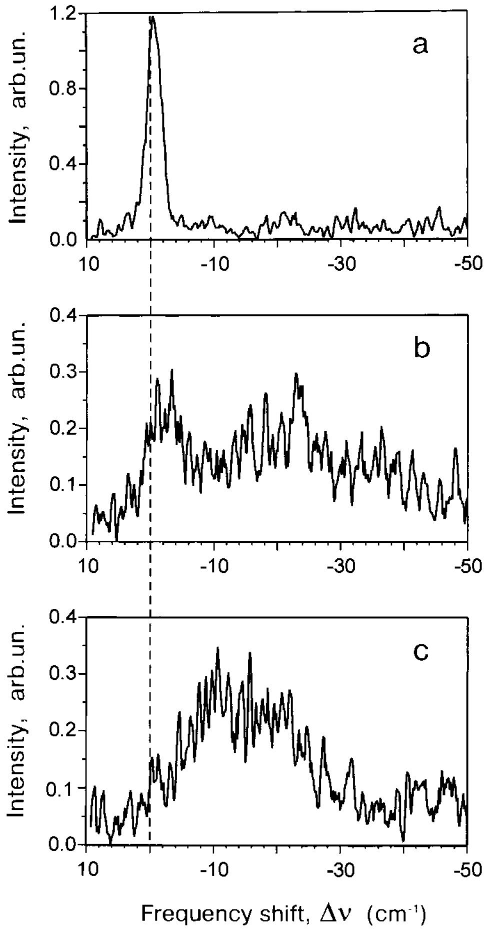

Figure 2. Stokes Raman spectra in the vicinity of the mode v_1 in SF_6: (a) prior to the passage of the exciting CO_2 pulse; (b) just after (τ_d = 25 ns) the end of the exciting pulse; (c) 3.5 μs after the end of the exciting pulse. $P_{SF_6} = 0.6$ Torr, 10P(16) CO_2 laser line, $\Phi = 0.7$ J/cm^2. (Intensity is given in arbitrary units that are the same for all three spectra.)

and rotational degrees of freedom still remain “cold”, for the time constant of the $V-T/R$ relaxation process ($p\tau = 122$ μs·Torr[24]) exceeds considerably the value of $p\tau_d$ selected by us. Note that in such conditions one can disregard the diffusion of the molecules out of the excitation region as well.

That the “equilibrium” spectrum measurement conditions selected are justified is also confirmed by the Stokes Raman spectra of the mode v_1 shown in Figure 2. (The Stokes spectra were chosen for illustration of population distribution because they, as distinct from anti-Stokes ones, represent both excited and unexcited molecules.) Figure 2a presents the spectrum of unexcited SF_6 molecules measured prior to the passage of the IR pulse. This is a narrow *Q*-branch, slightly asymmetric because of the presence of “hot” bands. Figure 2b shows an “instantaneous” spectrum of the mode v_1 obtained immediately ($\tau_d \approx 25$ ns) after the passage of the laser pulse. One can readily see that it is highly disturbed, shifted toward the red side, and possesses a distinct bimodal structure. The latter reflects the highly nonequilibrium, bimodal character of the population distribution function formed in the course of IR MP excitation. The bimodal character of vibrational distribution in SF_6 was earlier observed in a number of works.[7,10,25] As for the reasons for such a distribution, see, for example, ref 9. The collisional vibrational relaxation process leads to the establishment of a single equilibrium vibrational distribution, as evidenced by the spectrum of Figure 2c measured at a time of $\tau_d = 3.5$ μs after the passage of the exciting IR pulse. (Note that the “jagged” character of the spectra in Figure 2b,c reflects mainly the photon counting statistics in the different channels of the multichannel spectroanalyzer.)

The subsequent measurements of “equilibrium” spectra of highly excited SF_6 molecules were taken in the anti-Stokes region, because the level of the background, parasitic illumination here was substantially lower. We measured the spectra of the mode v_1 after exciting the molecules on various CO_2 laser lines and at various values of the energy fluence Φ in order to cover a sufficiently wide range of T_{vib} values. (The Φ values were always selected to lie below the IR MPD threshold, so that the dissociation of the SF_6 molecules could be avoided.) Figure 3 presents some of the spectra measured. The vibrational temperature T_{vib} for these spectra (measured as described above) ranges between 850 and 1660 K. The first fact following from Figure 3 is that even for highly excited molecules the Raman spectrum is localized near the frequency of mode v_1. On the other hand, as might be expected, the spectrum of the excited molecules is shifted toward the red side because of vibrations’ anharmonicity, and the higher the temperature (energy) of the molecules, the greater this shift. The analysis of the spectra obtained is presented below.

3. Comparison between Experimental and Theoretical Spectra

3.1. Model. As noted in the Introduction, it is assumed that the character of vibrational transitions from some given state in the quasicontinuum depends on two main types of broadening. These are homogeneous and inhomogeneous broadening. The latter, the statistical inhomogeneous broadening, has been considered in detail in our work.[21] Therefore, we will restrict ourselves here to a brief exposition of the information necessary later on.

We will consider optical transitions near the frequency of one of the *s* modes of a molecule (referred to as the “active” mode v_a) from some vibrational state $|g_\alpha\rangle$ with an energy of E_{vib}. [The remaining $s - 1$ modes v_i ($i \neq$ a) are as usual taken to be the bath modes.] It has been assumed in ref 21 that the states $|g_\alpha\rangle$ have a great number of projections on the regular states $|h_\beta\rangle$:

$$|g_\alpha\rangle = \sum_\beta c_{\beta\alpha}|h_\beta\rangle \tag{3}$$

This means that within some energy interval δE the states $|h_\beta\rangle$ with closely similar energies E_β in the vicinity of E_{vib} are mixed to yield in the final result the eigenstate $|g_\alpha\rangle$. The energy of the states $|h_\beta\rangle \equiv |n_1, ..., n_s\rangle$ may be represented in the form

$$E_\beta \approx \sum_{i=1}^{s} n_i[v_i + x_{ii}(n_i - 1)] + \sum_{i=1}^{s}\sum_{j=1}^{i-1} x_{ij}n_in_j \tag{4}$$

where x_{ij} are anharmonicity constants. Furthermore, if we are interested in the spectrum of transitions from the state $|g_\alpha\rangle$ in the neighborhood of the frequency of the mode v_a, we must consider *all* the possible transitions to the other eigenstates differing from the original one by approximately v_a. However, it has been shown in ref 21 that in the case of sufficiently slow IVR, one may restrict oneself to the account of the transitions between the regular states, $|h_\beta\rangle \rightarrow |h_\beta{}^+\rangle$ (upward transitions), involving a unit change in the occupation number n_a in the active mode *only*. In that case, the line intensity for the upward transitions from the state $|h_\beta\rangle$ with the energy E_β will be

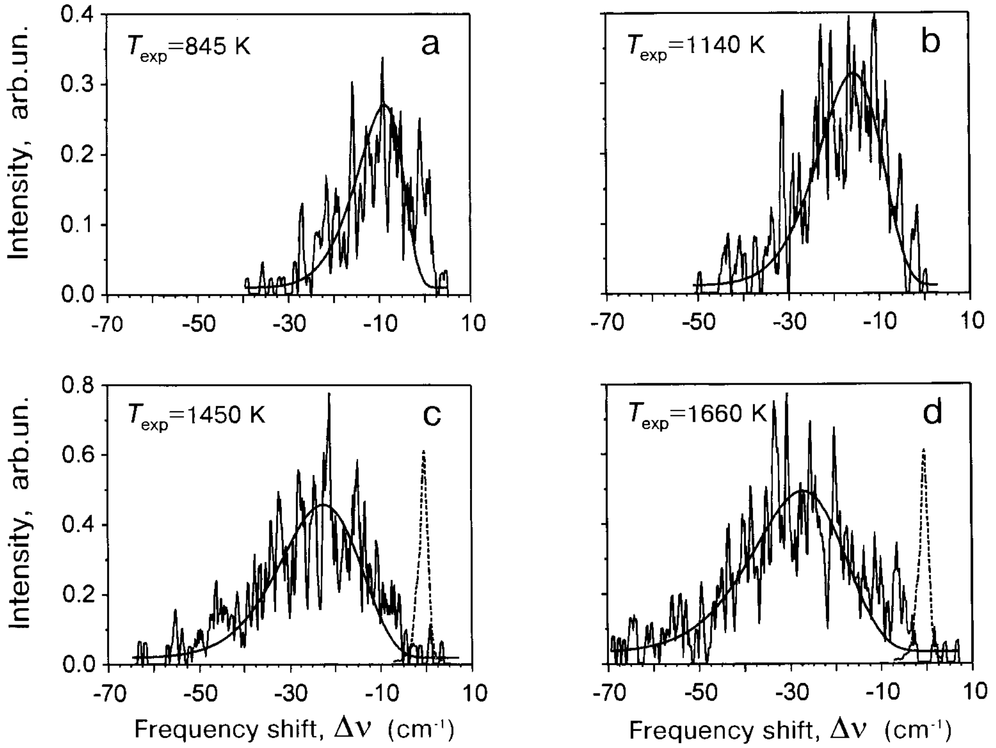

Figure 3. Anti-Stokes Raman spectra of excited SF$_6$ molecules at various vibrational temperatures. Smooth curves, model calculation; thin dashed line, spectrum at $T = -47$ °C (intensity is strongly magnified). (a) $T_{exp} = 845 \pm 25$ K, $T_{mod} = 865$ K, $\langle n_1 \rangle = 0.365$, 10P(12) CO$_2$ laser line, $\Phi = 1.08$ J/cm^2; (b) $T_{exp} = 1140 \pm 35$ K, $T_{mod} = 1127$ K, $\langle n_1 \rangle = 0.603$, 10P(24) CO$_2$ laser line, $\Phi = 0.57$ J/cm^2; (c) $T_{exp} = 1450 \pm 40$ K, $T_{mod} = 1430$ K, $\langle n_1 \rangle = 0.865$, 10P(24) CO$_2$ laser line, $\Phi = 0.86$ J/cm^2; (d) $T_{exp} = 1660 \pm 45$ K, $T_{mod} = 1628$ K, $\langle n_1 \rangle = 1.05$, 10P(16) CO$_2$ laser line,$\Phi = 1.02$ J/cm^2. All measurements are taken at $p\tau_d = 2.1$ μs·Torr.

$$I_\beta^{\,+} \sim n_a + 1 \tag{5}$$

The frequency of such a transition will be shifted, because of anharmonicity, relative to the frequency $\nu_a^{(0)}$ of the unperturbed transition $0 \rightarrow 1$. The magnitude of this shift $\Delta\upsilon_a$ can be found from the well-known expression

$$\Delta\upsilon_a = 2x_{aa}n_a + \sum_{i\neq a} x_{ai}n_i \tag{6}$$

Thus, each set $\{n_i\}$ of occupation numbers in eq 4 corresponds to a certain $\Delta\upsilon_a$ value and hence a certain transition frequency. The fact that the eigenstate $|g_\beta\rangle$ is formed by a great number of the states $|h_\beta\rangle$ results in that there arise a great number of transitions instead of a single one, each having a frequency of its own in accordance with eq 6. The dispersion of the occupation numbers in eq 4 makes the frequencies of the corresponding transitions disperse. And it is the dispersion of transition frequencies that is the cause of the statistical inhomogeneous broadening.

The above ideas form the basis of a numerical method for calculating the principal parameters of transitions in the quasicontinuum, such as the shape, width, and intensity of the transition profile and the position of its maximum. The method uses relations similar to eqs 4−6, as well as the known literature data on the mode frequencies and anharmonicity constants x_{ij}. In these calculations, the first to be found are the line frequencies and intensities for transitions from a given state, due regard being given, if necessary, for the splitting of degenerate states. Next the histograms thus obtained are convolved with some "spread" function to obtain the shape of the transition profile. Specifically, the above parameters were calculated in this way for *upward* transitions in the vicinity of the modes υ_1 and υ_3 in the SF$_6$ molecule. It should be noted that the calculated transition band profiles can be described very well by the Gaussian function

$$I_\upsilon(\upsilon) = \frac{I_0}{\sigma_0\sqrt{2\pi}} \exp\left[-\frac{(\upsilon - \upsilon_0)^2}{2\sigma_0^2}\right] \tag{7}$$

TABLE 1: Frequencies and Anharmonicity Constants of SF$_6$ Used for Calculations of Transition Profiles, Presented by Figure 4

	mode (i)					
	1	2	3	4	5	6
ν_i (cm^{-1})	774.54[a]	643.35[a]	948.10[b]	615.02[a]	523.56[a]	346.08[a]
x_{1i} (cm^{-1})	−0.896[c]	−2.358[c]	−2.902[c]	−1.144[c]	−1.12[c]	−0.3625[c]

[a] Taken from ref 27. [b] Taken from ref 28. [c] Taken from ref 29.

Using the above approach, we calculated similar parameters for *downward* transitions (anti-Stokes) in the neighborhood of the mode υ_1. The same set of frequencies and anharmonicity constants as in ref 21 was used in these calculations (see Table 1). The transition-line histograms obtained were then convolved with some smooth spread function. This was a Gaussian function with a half-width of $\sigma_{sp} = 0.98$ cm^{-1} (see below). The resultant transition profiles for vibrational energy values of 7000, 15 000, and 30 000 cm^{-1} are shown in Figure 4. It can be seen that as the vibrational energy of the molecule is increased, the transition band profile broadens substantially, and its maximum frequency υ_0 shifts toward the red side. This broadening is great enough: at the energy $E_{vib} = 30\,000$ cm^{-1} the bandwidth $2\sigma_0$ reaches some 14 cm^{-1}. Note that the shape of the profiles obtained is adequately described by the Gaussian function in eq 7 (circles in Figure 4b,c). The resultant shape of transition profiles was also shown to be independent of the type of

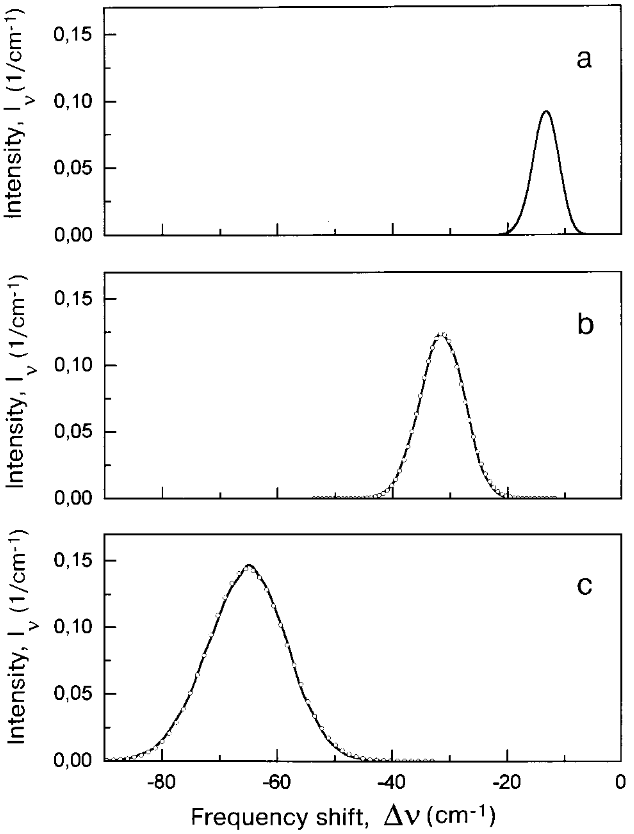

Figure 4. Calculated band profile (solid lines) of the anti-Stokes transitions in the vicinity of the frequency of the mode υ_1 of SF$_6$ for various values of the initial energy $E_{\rm vib}$: (a) 7000 cm^{-1}; (b) 15 000 cm^{-1}; (c) 30 000 cm^{-1}. (○) Approximation by a Gaussian function.

smoothing "spread" function used (see also ref 21). As to the integral band intensity, the values obtained coincide, as expected, with $I = I_0\langle n_1\rangle$ to a high degree of accuracy, where I_0 is the intensity of the transition 0 → 1 and $\langle n_1\rangle$ is the occupation number in the mode υ_1 at a given energy $E_{\rm vib}$. On the basis of our calculated data, we obtained the following approximation for energy dependences of the position of the profile maximum υ_0 (measured from the unperturbed frequency υ_1) and its half-width σ:

$$\upsilon_0(E_{\rm vib}) = 2.2095 - (2.245 \times 10^{-3})E_{\rm vib} \tag{8}$$

$$\sigma(E_{\rm vib}) = 0.8245 + (1.981 \times 10^{-4})E_{\rm vib} \tag{9}$$

Equations 8 and 9 were later used to adjust the experimental spectra.

3.2. Fitting Procedure. The essence of the fitting procedure is to find such a model spectrum shape as approximates the actually measured spectrum envelope in an optimal (by some criteria) fashion. The fitting procedure is as follows (for more details, see ref 26). The intensity $J(\Delta\upsilon_j)$ of a Raman spectrum at some "observation" point j detuned by an amount $\Delta\upsilon_j$ from the frequency of the undisturbed transition in the mode υ_1 may be expressed as

$$J(\Delta\upsilon_j) = J_0\sum_k\langle n_1(E_k)\rangle\, G(E_k, \Delta\upsilon_j)F(E_k, T) \tag{10}$$

Equation (10) is the sum of the contributions to the signal intensity at the point j from the quasicontinuum states with an energy of E_k. The parameter $\langle n_1(E)\rangle$—the average value of the occupation number in the mode υ_1—determines the integral band intensity, and $G(E_k,\Delta\upsilon_j)$ is the band shape defined by eq 7 with the parameters $\upsilon_0(E)$ and $\sigma(E)$ defined by eqs 8 and 9, respectively. The function $F(E_k, T) = \rho(E_k)\exp(-E_k/kT)$, where $\rho(E_k)$ is the density of vibrational states, reflects the Boltzmann character of the vibrational distribution [the function $\rho(E_k)$ was calculated in the well-known Whitten−Rabinovitch approximation, which was proved[26] to be adequate for the present task]. The states E_k in the quasicontinuum were taken at 500 cm^{-1} intervals. Reducing this interval had no effect on the shape of the spectrum calculated.[26]

The sought-for model spectrum was found by the least-squares method; i.e., it was the minimum of the function

$$f_2 = \sum_j (J_j^{\rm mod} - J_j^{\rm exp})^2 \tag{11}$$

that was looked for subject to the additional condition that the sum of deviations was equal to zero:

$$f_1 = \sum_j (J_j^{\rm mod} - J_j^{\rm exp}) = 0 \tag{12}$$

where eq 12 is the spectrum intensity conservation condition. The variable parameters were J_0 and T, the vibrational temperature T being taken to agree with the experimentally measured values within the experimental error (see caption to Figure 3).

Note also that the spread function of the instrument itself, as well as the rotational width of the Q-branch in the fitting procedure described, also proved to be accounted for, because the effective spread function used in finding the parameters $\upsilon_0(E)$ and $\sigma(E)$ was an approximation of the actual anti-Stokes spectrum measured prior to the passage of the exciting pulse.

The model spectra obtained are presented in the form of smooth curves in Figure 3.

4. Discussion

Comparison between the experimental spectra and their model counterparts presented in Figure 3 shows that the latter describe the observed, actual spectra well enough in a sufficiently wide temperature interval—from 850 to 1660 K. Note that this temperature interval corresponds to a change in the *average* energy of the molecules from some 5700 cm^{-1} to 12 800 cm^{-1}. The average occupation number $\langle n_1\rangle$ in the υ_1 mode changes in this case from 0.365 up to 1.05. The model spectra predict well enough the position of the maximum of the spectrum, the vibrational temperatures found for the "best fitting" spectra being in agreement with the experimentally measured values to within the experimental error. All this allows us to conclude that the method developed in ref 21 for calculating the spectral characteristics of transitions in the quasicontinuum, based on the consideration of the statistical inhomogeneous broadening effect, makes it generally possible to describe well enough actual spectra of highly excited quasicontinuum states, when SIB plays the predominant role, as is demonstrated by Raman spectra of the υ_1 mode of SF$_6$ molecule.

Nevertheless, there are some differences between the experimental and theoretical spectra. The top of the experimental spectra is somewhat flatter, and the highly excited part (the region of high $\Delta\upsilon$ values) in them drops more slowly than in their model counterparts. There are also some differences in the low-energy part of the spectra—the region of low $\Delta\upsilon$ values in Figure 3. Let us discuss the possible causes of these differences. They can be subdivided into two groups. The first is associated with some specifics of taking measurements and of model calculations themselves. The second group is associated with the possible failure to take account of some principal factors, the homogeneous broadening for one.

Let us first dwell upon the first group. Note at once that the model calculations performed are not correct enough in the low-energy region, for the functions $\nu_0(E)$ (eq 8) and $\sigma(E)$ (eq 9) were extrapolated down to $E = 774$ cm^{-1}, i.e., to $\Delta\nu_i = 0$. Nevertheless, the extrapolation of eqs 8 and 9 down to 2500−3000 cm^{-1} for "thermal" spectra is apparently adequate enough. There are another two factors associated with the taking of measurements, which may influence the degree of agreement between theory and experiment. First, the experimental spectra were obtained upon accumulation of a great number of pulses, and for this reason, fluctuations of the pump pulse intensity, and hence of the excitation level of the molecules, may lead to a certain additional "broadening" of the spectra obtained. In principle, this factor can be eliminated, provided the experimental spectra are "sorted out" in accordance with the pump pulse energy. A more important (and principal) factor is, in our view, the question of the possible "incomplete" relaxation of the molecules by the moment τ_d when the probing pulse arrives. As noted earlier, with the quantity $p\tau_d$ being taken equal to 2.1 μs·Torr, relaxation must have come to an end. Nevertheless, the original distribution being of strongly nonequilibrium character (the bimodal distribution of Figure 2b), some lack of equilibrium may still remain, especially at the tail of the distribution.

The second group of causes of the discrepancy between the experimental and theoretical spectra may be associated with failure to take account of some principal factors. It primarily includes neglect of the homogeneous broadening. As noted earlier, in the case of the mode ν_3 in SF$_6$, the magnitude of this type of broadening is much smaller than that of the inhomogeneous broadening. As follows from the results obtained in the present work, the contribution from the homogeneous broadening to the total width of the transition profile in the case of the mode ν_1 is also apparently smaller than that from the SIB or, in any case, does not exceed it: increasing the width of transition profiles by 30−50% causes the model spectra to broaden substantially in comparison with their experimental counterparts. In principle, by introducing an additional Lorentzian transition profile width to model the homogeneous broadening, one can attain a better agreement between the experimental and model spectra, which will in turn enable one to estimate the magnitude of the homogeneous broadening. However, by virtue of the insufficient quality of the measured spectra (strong fluctuations of the numbers of counts in the individual channels of the multichannel photon counter) and the possibility noted above of an "experimental" broadening of the spectra, we think that such estimates will as yet be not very reliable. Improving the accuracy of measurements will allow us to return to this problem.

Finally, it should be noted that we have used in this paper the harmonic approximation for calculation of the position of vibrational levels (eq 10 and the results of Figure 4). This approximation is quite adequate for the present quality of the experimental data, because the anharmonic correction to, e.g., $\nu_0(E_{vib})$ (eq 8) and $\sigma(E_{vib})$ (eq 9) parameters was shown[21] not to exceed a few percent in the temperature range used.

5. Conclusions

Our measurements of the Raman spectra of highly excited SF$_6$ molecules have shown that even for molecules residing high in the quasicontinuum, the spectrum remain sufficiently structured, localized in the vicinity of the frequency of the unperturbed transition, near the position of the mode ν_1 in our case. At the same time, as the temperature (energy) of the molecule is increased, the spectrum gets deformed: it broadens, and its maximum shifts toward the red side. Using the numerical method developed earlier, we have calculated the main parameters (profile shape, position of the maximum, and intensity) of vibrational transitions in the quasicontinuum in the neighborhood of the mode ν_1 in SF$_6$ and their dependence on the energy of the molecule in an approximation where these parameters are governed by the *statistical inhomogeneous broadening*. On the basis of the parameters found, we have calculated the anti-Stokes Raman spectra near the mode ν_1 of SF$_6$ for various vibrational temperatures of the molecule. A good agreement has been achieved between the experimental and theoretical spectra throughout the temperature range used (850−1660 K). We have concluded that as in the case of the mode ν_3, the main contribution to the spectrum width of the ν_1 transitions in the quasicontinuum apparently comes from the statistical inhomogeneous broadening and not from the homogeneous broadening.

Thus, our experiments and model calculations allow us to conclude that the method developed in ref 21 for calculating spectral parameters of transitions is capable of describing actual spectra well enough in cases where the statistical inhomogeneous broadening is dominant.

Acknowledgment. This work was partially supported by the Russian Foundation for Basic Research, Grant 96-02-17278.

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