

Relaxation of vibrational nonequilibrium distributions: the effect of multiphoton excitation on relaxation behavior

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Abstract A theoretical study has been made on the non-stationary relaxation of highly vibrationally excited molecules in the presence of a source, producing these molecules. Initially, the nonequilibrium vibrational distribution is created using multiphoton absorption of laser radiation. An exact, analytical solution to the master equation is derived in terms of Meixner polynomials with regard to VV- and VT-processes. The time-dependent distribution of the system “molecule + field” is used to give explicit expressions for the mean number of photons distributed among vibrational and translational degrees of freedom and for the time dependence of average energy transferred per collision.

Keywords Vibrational relaxation · Energy transfer · Transition probability · Multiphoton absorption · Meixner polynomials

1 Introduction

Traditionally, the multiphoton excitation of molecules is considered in collisionless regime [1–5] and the influence of collisions is discussed as an interesting but unwanted side effect [6]. In the present work, we are dealing with this problem quite differently. The relaxation of highly vibrationally excited molecules, produced by external source, is examined in detail. The excited molecules arise from the source due to the multiphoton absorption of laser radiation. The vibrational relaxation of polyatomic molecules is treated over the entire time-scale, including the non-stationary stage which directly

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follows the switching of the source. This stage may be of interest for studying the pulse methods of excitation when either pulse duration is comparable with vibrational relaxation time or the source operates continuously. The vibrationally excited molecules originate from a pump laser. Note that upon laser excitation the initial distribution is strongly non-equilibrium.

As previously [1–6], the energy molecule spectrum is conditionally partitioned into three groups: the system of lower vibrational levels, the quasicontinuum of highly excited states, and the true continuum of the states lying above the dissociation limit. It has been universally accepted that the multiphoton absorption proceeds coherently in the first few levels and incoherently in the latter levels [1,2]. Only the incoherent absorption can be described by the set of first-order linear differential equations for the course-grained levels of a polyatomic molecule. The excitation energy of a molecule is randomized over all vibrational modes before its decomposition, and a statistical approach is suited well for the description of collisional dynamics in the laser field. It is assumed that the absorption is incoherent up from the first step, and the losses by dissociation can be neglected. Therefore, the problem of lower levels is solved here by introducing the probability of populating the vibrationally excited states. In the framework of this approach, we are going to offer an analytical model with an exact solution.

2 The master equation and its solutions

Consider now the admixture of the vibrationally excited molecules of kind a in a heat bath of atoms b . For our purpose, of most interest are the polyatomic molecules, arising in the highly vibrationally excited states under the action of the laser field. The vibrational states are partitioned into degenerate levels of the equal energy spacing, $n h \nu$, where ν is the laser frequency [1–6]. In other words, only these levels will be populated due to energy conservation in the system “molecule + field”. The dipole moment is non-zero only for transitions between neighboring levels. It is assumed then that the degeneracy factor is the number of ways to distribute n quanta between s identical oscillators without restrictions

$$g_s(n) = \binom{n+s-1}{n} \quad (1)$$

The thermal distribution of the s -fold degenerate harmonic oscillator is of the form

$$\rho_n(\theta) = (1 - e^{-\theta})^s g_s(n) e^{-n\theta}, \quad (2)$$

where $\theta = h\nu/k_B T$. At thermal equilibrium, the mean number of photons per molecule is

$$\langle n \rangle_T = \frac{s}{e^\theta - 1} \quad (3)$$

Obviously, the mean thermal energy of the molecule is $h\nu \langle n \rangle_T$.

If $N_n(t)$ is the time-dependent population, i.e., the fraction of excited molecules in level n at time t , the populations satisfy the master equation [7,8]

$$\begin{aligned} \dot{N}_n(t) = & \sum_{n'=0}^{\infty} \left[\left(v_{aa} P_{n' \rightarrow n}^{aa} + v_{ab} P_{n' \rightarrow n}^{ab} \right) N_{n'}(t) - \left(v_{aa} P_{n \rightarrow n'}^{aa} + v_{ab} P_{n \rightarrow n'}^{ab} \right) N_n(t) \right] \\ & + v_{aa} \sum_{m, m', n'=0}^{\infty} \left[P_{n' \rightarrow n}^{m' \rightarrow m} N_{m'}(t) N_{n'}(t) - P_{n \rightarrow n'}^{m \rightarrow m'} N_m(t) N_n(t) \right] + \dot{Q}_n(t) \quad (4) \end{aligned}$$

The dot denotes differentiation with respect to time. Here v_{ab} is the collision frequency of the molecule of interest with species a and b , respectively. Expression in the first brackets describes the processes of vibrational-translational (VT) energy transfer with the probabilities $P_{n' \rightarrow n}^{ab}$. Expression in the second brackets refers to the vibrational-vibrational (VV) quantum exchange between molecules. The rate of excited molecule production is set by the term $\dot{Q}_n(t)$, where $Q_n(t)$ is the probability of populating the n th level at time t . In another way, this is the absorption probability of n photons during this time.

Solution to Eq. (4) for the arbitrary initial conditions may be written in terms of the Green function $G(n', t'; n, t)$. Physically, it is the density of conditional probability to find the random energy $E(t)$ equal to E_n at time t provided it was $E_{n'}$ at previous time t' . When the laser is turned on at $t = 0$, the molecules start to move up the energy ladder without appreciable dissociation. Then, a general solution to the master equation obeys the equation

$$N_n(t) = \sum_{n'=0}^{\infty} \left[N_{n'}(0) G(n', 0; n, t) + \int_0^t \dot{Q}_{n'}(t') G(n', t'; n, t) dt' \right], \quad (5)$$

where $G(n', t'; n, t) = \delta_{n'n}$. As is seen, to determine the required population, the Green function should be calculated using a satisfactory model of all probabilities. Further, a general solution to Eq. (4) will be found as the expansion in terms of orthogonal polynomials. The Meixner polynomials of a discrete variable will be a suitable tool for studying the vibrational relaxation of s -fold degenerate harmonic oscillators. The Appendix presents useful formulas, including these polynomials.

Here we will seek for the Green function, neglecting the laser field effect on collisional probabilities. The probabilities are adiabatically small due to the large value of vibrational quantum. The first-order perturbation theory provides probabilities of only the one-quantum transitions that are well known in the harmonic approximation [7–10]. The probabilities of downward transitions are left unchanged

$$P_{n \rightarrow n-1} = n P_{10} \quad \text{and} \quad P_{n+1 \rightarrow n} = (n+1) P_{10} \quad (6)$$

The probabilities of upward transitions are determined from the principle of detailed balance

$$P_{n-1 \rightarrow n} = \frac{g_s(n)}{g_s(n-1)} e^{-\theta} P_{n \rightarrow n-1} = (n+s-1)e^{-\theta} P_{10} \tag{7}$$

and

$$P_{n \rightarrow n+1} = \frac{g_s(n+1)}{g_s(n)} e^{-\theta} P_{n+1 \rightarrow n} = (n+s)e^{-\theta} P_{10} \tag{8}$$

The well-known probabilities of the VV-processes may be also generalized in terms of the perturbation theory

$$P_{n \rightarrow n-1}^{m \rightarrow m+1} = \frac{n(m+s)}{s} P_{01}^{10} = \frac{n(m+s)}{(m+1)(n+s-1)} P_{n-1 \rightarrow n}^{m+1 \rightarrow m} \tag{9}$$

and

$$P_{n+1 \rightarrow n}^{m-1 \rightarrow m} = \frac{(n+1)(m+s-1)}{s} P_{01}^{10} = \frac{(n+1)(m+s-1)}{(n+s)m} P_{n \rightarrow n+1}^{m \rightarrow m-1} \tag{10}$$

It will now be assumed that the fraction of excited molecules in the heat bath is small (but not infinitely small) and the amount of energy absorbed by them is sufficiently small so that the heat bath will remain to within a good approximation at its initial temperature T . By introducing Eqs. (6)–(10) into the master equation, we obtain

$$\begin{aligned} \dot{G}_n(t) = & - [n\omega + (2n+s)\Omega(n', t)] G_n(t) + (n+1) [\omega + \Omega(n', t)] G_{n+1}(t) \\ & + (n+s-1)\Omega(n', t) G_{n-1}(t) \end{aligned} \tag{11}$$

For brevity, the $G(n', 0; n, t)$ is designated by $G_n(t)$. Let us specify the other notations in Eq. (11). In particular, the transition probabilities per unit time up and down at one quantum are given in terms of the characteristic “frequency”

$$\Omega(n', t) = \frac{1}{s} [\varpi \langle n \rangle_T + (\omega - \varpi) \langle n(n', t) \rangle] \tag{12}$$

It depends on the initial quantum number n' at $t = 0$. The decay rate of excited states is specified by the mean time $1/\varpi$, where

$$\varpi = \frac{\nu_{aa}}{Z_V^{aa}} + \frac{\nu_{ab}}{Z_V^{ab}} \tag{13}$$

In Eq. (13), the mean number of collisions is given by the relation

$$\frac{1}{Z_V^{ab}} = P_{10}^{ab} (1 - e^{-\theta}) \tag{14}$$

Accounting for the resonance VV-processes along with the VT- processes results in one more characteristic time $1/\omega$, where

$$\omega = \overline{\omega} + \nu_{aa} P_{01}^{10} \quad (15)$$

The time-dependent average vibrational energy (without laser field) is defined via the first moment

$$\langle \langle n(n', t) \rangle \rangle = \sum_{n=1}^{\infty} n G(n', 0; n, t) \quad (16)$$

It is worth noting that this average depends on the initial quantum number and appears due to collisions. It is designated by double brackets to distinguish it from the mean number of photons $\langle n(t) \rangle$ absorbed per molecule, which is non-zero under collisionless excitation conditions.

The first moment may be determined from Eq. (11) by working out an equation for $\langle \dot{n}(n', t) \rangle$. To this end, Eq. (11) is multiplied by n and summed over all n . This simple problem is solved as follows

$$\langle \langle n(n', t) \rangle \rangle = \langle n \rangle_T + (n' - \langle n \rangle_T) e^{-\overline{\omega} t} \quad (17)$$

By definition, the first moment is initially n' and tends to the equilibrium value at large times. As can be seen, it is exponential in time and independent of VV exchange processes.

The set of differential difference Eq. (11) may be solved by generating function method. Let us consider a generating function

$$F(z, t) = \sum_{n=0}^{\infty} z^n G_n(t) \quad (18)$$

Using its partial derivatives with respect to t and z , we get the partial differential equation

$$\frac{\partial F}{\partial t} - \left[\omega(1-z) + \Omega(n', t)(1-z)^2 \right] \frac{\partial F}{\partial z} = -s\Omega(n', t)(1-z)F \quad (19)$$

The method of characteristics is used to write Eq. (19) as a system of ordinary differential equations

$$-dt = \frac{dz}{\omega(1-z) + \Omega(n', t)(1-z)^2} = \frac{dF}{s\Omega(n', t)(1-z)F} \quad (20)$$

Solution to the first equation (one of these two) is found quite easily in the form

$$C_1 = \left[\frac{1}{1-z} + a(n', t) \right] e^{\omega t}, \quad (21)$$

where C_1 is the constant of integration, and the $a(n', t)$ function is given by

$$a(n', t) = \int_0^t e^{-\omega(t-t')} \Omega(n', t') dt' \tag{22}$$

An explicit expression for $a(n', t)$ may be derived by substituting Eq. (12) into (22) and using Eq. (17)

$$a(n', t) = \frac{1}{s} [\langle n(n', t) \rangle - n' e^{-\omega t}] \tag{23}$$

This function is zero at $t = 0$, whereas at $t \gg 1/\omega$, when the VV-processes are over, it tends to the mean number of photons per mode.

As is readily verified by substitution, a solution to the second equation is

$$F(z, t) = \frac{C_2}{[1 + a(n', t)(1 - z)]^s}, \tag{24}$$

where C_2 is the second constant of integration which represents an arbitrary $\varphi(C_1)$ function. By definition, at $t = 0$ the generating function is equal to $z^{n'}$. According to Eqs. (21) and (24) this function should be chosen as follows

$$C_2 = \phi(C_1) = \left(1 - \frac{1}{C_1}\right)^{n'} \tag{25}$$

It is appropriate to introduce here the functions $e^{-\alpha}$ and e^β , defined by the equations:

$$e^{-\alpha} = \frac{a(n', t)}{1 + a(n', t)}, \tag{26}$$

$$e^{-\alpha+\beta} = \frac{a(n', t) - e^{-\omega t}}{1 + a(n', t) - e^{-\omega t}} \tag{27}$$

To avoid cumbersome formulas, we omit the t argument in the $\alpha(t)$ and $\beta(t)$ functions. The final result is obtained by simple algebraic manipulations

$$F(z, t) = \left(\frac{1 - e^{-\alpha}}{1 - ze^{-\alpha}}\right)^s \left(\frac{1 - e^{-\alpha}}{1 - e^{-\alpha+\beta}}\right)^{n'} \left(\frac{1 - ze^{-\alpha+\beta}}{1 - ze^{-\alpha}}\right)^{n'} \tag{28}$$

The required solution to $G_n(t)$ is of the form

$$G(n', 0; n, t) = \rho_n(\alpha) \left(\frac{1 - e^{-\alpha}}{1 - e^{-\alpha+\beta}}\right)^{n'} \frac{e^{n'\beta/2}}{\sqrt{g_s(n')}} M_{n'}(n, \beta) \tag{29}$$

Here $M_{n'}(n, \beta)$ are the Meixner polynomials of a discrete variable n (see the Appendix). Formula (57) makes it possible to confirm that substituting Eq. (29) into (18)

gives exactly Eq. (28). Obviously, the Green function is normalized to unity for any initial conditions. Numerical calculations are convenient to perform using the expression into which the Meixner polynomials should be substituted according to Eq. (51):

$$G(n', 0; n, t) = \frac{g_s(n)[a(n', t)]^n (1 + a(n', t) - e^{-\omega t})^{n'}}{[1 + a(n', t)]^{n+n'+s}} \tag{30}$$

$$\times \sum_{k=0}^{n_<} \frac{1}{g_s(k)} \binom{n}{k} \binom{n'}{k} \left\{ \frac{e^{-\omega t}}{a(n', t) [1 + a(n', t) - e^{-\omega t}]} \right\}^k$$

where $n_< = \min(n', n)$. We see that an exact solution to Eq. (11) is given in terms of the finite sum of elementary functions. By simple reasoning it is possible to demonstrate that $G(n', 0; n, 0) = \delta_{nn'}$. Since $a(n', t) \propto t$ at $t \rightarrow 0$, then the hypergeometric series diverges as $t^{-2n_<}$. Thus, the $t^{|n-n'|}$ solution differs from zero at $t = 0$ for $n = n'$ only. Finally, the Green function, depending on time t' , is of the form

$$G(n', t'; n, t) = G(n', 0; n, t - t') \tag{31}$$

The probability of transition from the (n', t') state to the (n, t) state depends on the time interval (a stationary Markov process) rather than on the two times.

Below we make some general comments. Let at $t = 0$ all the molecules be in the ground state. Equation (29) then takes on the $\rho_n(\alpha)$ form for $t > 0$. The system relaxes to the final Boltzmann distribution at temperature T via a continuous sequence of Boltzmann distributions with a vibrational temperature $T_V = h\nu/k_B\alpha$. It is obvious that $\alpha(\infty) = \theta$. Let us consider for example the case $n' = 1$. From Eq. (29) we get

$$G(1, 0; n, t) = \rho_n(\alpha) \left(\frac{1 - e^{-\alpha}}{1 - e^{-\alpha+\beta}} \right) \left[1 + \frac{n}{s} (1 - e^\beta) \right] \tag{32}$$

It is seen that the population is far from the Boltzmann distribution at $\beta \neq 0$. Therefore, it cannot be characterized by the time-dependent vibrational temperature which holds for other $n' \neq 0$ because of the complementary $\beta(t)$ function. It is of particular interest that the $\beta(t)$ function turns into zero at $t \rightarrow \infty$ faster than the $\alpha(t) - \theta$ function, i.e., $\beta(t) \approx 0$, but $\alpha(t) \neq \theta$. This distinction is due to the fact that the rates of the resonance VV- processes substantially exceed those of the adiabatic VT-processes. Thus, the difference between the exponents $e^{-\omega t}$ and $e^{-\omega' t}$ may be of many orders of magnitude. Consider the case, where the VV-processes are already over, i.e., $e^{-\omega t} \approx 0$, but $e^{-\omega' t} \neq 0$. With $t \gg 1/\omega$ the solution reduces to

$$G(n', 0; n, t) \approx \rho_n(\alpha), \tag{33}$$

where

$$e^{-\alpha} \approx \frac{\langle n(n', t) \rangle}{s + \langle n(n', t) \rangle} \tag{34}$$

In another way, the solution is determined by the time-dependent mean number of photons per mode. The system is restored to its equilibrium state at large times, which is demonstrated by Eqs. (33) and (34).

3 The time-dependent average energy and energy transfer

Now we calculate the average energy transferred per collision

$$\langle \Delta E(n) \rangle = \sum_{n'=0}^{\infty} (E_{n'} - E_n) \left((1-x) P_{n \rightarrow n'}^{aa} + x P_{n \rightarrow n'}^{ab} \right), \quad (35)$$

where $x = \nu_{ab}/(\nu_{aa} + \nu_{ab})$ is the fraction of buffer atoms. The energy transfer is readily calculated for one-quantum transitions

$$\langle \Delta E(n) \rangle = -\frac{E_n - \langle E \rangle_T}{Z_V}, \quad (36)$$

where $\langle E \rangle_T$ is the mean thermal energy, and Z_V is the mean number of collisions necessary to reach equilibrium

$$\frac{1}{Z_V} = \frac{x}{Z_V^{ab}} + \frac{1-x}{Z_V^{aa}} \quad (37)$$

It is seen that the energy excess $E_n - \langle E \rangle_T$ is transferred to the heat bath in Z_V steps with the step size equal to $\langle \Delta E(n) \rangle$. For the highly excited molecule, a collision ends, on the average, in energy loss only; therefore, the average energy transfer is negative for the high vibrational energies.

It is clear that the perturbation theory works well for weak collisions, i.e., $Z_V \gg 1$. The large value of the vibrational quantum, $h\nu$, provides the exponentially small probability P_{10} [10]. Therefore, Z_V varies from 10^1 to 10^4 for polyatomic molecules [11]. Note that Z_V increases with increasing temperature.

We have got the $N_n(t)$ distribution to calculate the ensemble averages for the system “molecule+ field”. Let us evaluate the mean number of photons, stored by molecules at the vibrational degrees of freedom in a time t

$$\langle \langle n_V(t) \rangle \rangle = \frac{\langle \langle E(t) \rangle \rangle}{h\nu} = \sum_{n=1}^{\infty} n N_n(t) \quad (38)$$

Here $\langle \langle E(t) \rangle \rangle$ is the average vibrational energy. Substituting $N_n(t)$ from Eq. (5) into (38), in conjunction with Eqs. (16) and (31), we get

$$\langle \langle n_V(t) \rangle \rangle = \sum_{n'=0}^{\infty} \left[N_{n'}(0) \langle \langle n(n', t) \rangle \rangle + \int_0^t \dot{Q}_{n'}(t') \langle \langle n(n', t-t') \rangle \rangle dt' \right] \quad (39)$$

Remember that the initial distribution was equilibrium, $\rho_{n'}(\theta)$, before the laser is turned on at time $t = 0$. Integration with respect to dt' is performed in a trivial way. Summing over n' yields

$$\langle\langle n_V(t) \rangle\rangle = \langle n \rangle_T + \langle n(t) \rangle - \langle\langle n_{VT}(t) \rangle\rangle, \quad (40)$$

where $\langle\langle n_{VT}(t) \rangle\rangle$ is the number of photons transferred to the translational degrees of freedom

$$\langle\langle n_{VT}(t) \rangle\rangle = \int_0^t \langle n(t') \rangle e^{-\varpi(t-t')} \varpi dt', \quad (41)$$

and $\langle n(t) \rangle$ is the mean number of photons absorbed per molecule in a time t . In other words, it is the first moment of the absorption probability of n photons during this time

$$\langle n(t) \rangle = \sum_{n=1}^{\infty} n Q_n(t) \quad (42)$$

Thus, we see that the number of photons absorbed per molecule is distributed between the vibrational and translational degrees of freedom. Remember that $h\nu\langle n \rangle_T$ is the mean thermal energy, i.e., the energy per molecule at $t = 0$.

Consider now the behavior of these quantities at large times (see below Fig. 4). The laser pulse has got a finite duration and the total number of absorbed photons $\langle n(\infty) \rangle$ remains finite. At large times, with all relaxation processes over, only the thermal equilibrium amount of photons is available on the vibrational degrees of freedom, i.e., $\langle\langle n_V(t) \rangle\rangle$ has the $\langle n \rangle_T$ limit. As a result, the number of photons $\langle\langle n_{VT}(t) \rangle\rangle$ tends to $\langle n(\infty) \rangle$. In another way, the laser pulse energy is fully transferred to the heat bath during a long period of time. Thus, the number of photons $\langle\langle n_V(t) \rangle\rangle$ starts with $\langle n \rangle_T$, reaches a maximum, and tends to $\langle n \rangle_T$ at long times. Actually, the number of photons at thermal equilibrium will be different at $t = 0$ and $t = \infty$. However, we neglect an increase in heat bath temperature.

In this analysis, we have omitted the dissociation of molecules when a molecule reaches a certain level in the continuum of states, lying above the dissociation limit, and decomposes into fragments. This assumption holds if one can distinguish two independent stages of the relaxation process. The first fast stage with a characteristic time of $1/\varpi$ corresponds to the vibrational relaxation, which ends before the decomposition of a noticeable fraction of molecules. The second slow stage includes the decomposition of molecules and is characterized by the time \bar{t} , necessary for a molecule to reach dissociative states [12]. With $\varpi\bar{t} \gg 1$, the second stage occurs following the relaxation of average energy to equilibrium.

The average energy transfer per molecule at time t is of the form

$$\langle\langle \Delta E(t) \rangle\rangle = \sum_{n=0}^{\infty} \langle \Delta E(n) \rangle N_n(t) \quad (43)$$

Substituting Eq. (36) into (43) and using Eq. (40), we derive the relation

$$\frac{\langle\langle\Delta E(t)\rangle\rangle}{h\nu} = -\frac{\langle n(t)\rangle - \langle\langle n_{VT}(t)\rangle\rangle}{Z_V} \quad (44)$$

Because of the competitive contribution of the laser field and VT collisions, the average energy transfer, as a function of time, has a maximum. Initially, the $\langle\langle\Delta E(t)\rangle\rangle$ is zero and decreases to zero at long times which means that at equilibrium there is no net energy transfer in the bulk system.

The macroscopic law of the temporal evolution of the average vibrational energy follows from Eqs. (40) and (44)

$$\frac{d}{dt} \langle\langle E(t)\rangle\rangle = \nu_c \langle\langle\Delta E(t)\rangle\rangle + h\nu \langle\dot{n}(t)\rangle \quad (45)$$

It is worth noting that ϖZ_V is equal to the total collision frequency $\nu_c = \nu_{aa} + \nu_{ab}$. In this case, the term $h\nu \langle\dot{n}(t)\rangle$ is proportional to $I(t)$, where $I(t)$ is the laser intensity (the temporal profile of the pump laser pulse) [1–4]. Equation (45) is the well-known result from the theory of stochastic processes without external sources of excited molecules [13]. For $\langle\dot{n}(t)\rangle = 0$, this equation is of general character and independent of any particular form of the transition probability [14, 15].

The second essential feature of Eqs. (40) and (44) suggests broad potentials for practical implementation. Let us draw up the following ratio

$$\frac{\langle\langle E(\infty)\rangle\rangle - \langle\langle E(t)\rangle\rangle}{\langle\langle\Delta E(t)\rangle\rangle} = Z_V \quad (46)$$

which is time-independent. Equation (46) defines the mean number of collisions that should be obtained from experiments. This behavior results directly from a special case where the microscopic quantity $\langle\Delta E(n)\rangle$ is a linear function of the initial energy E_n (see Eq. (36)). Every time when $\langle\Delta E(n)\rangle$ is proportional to E_n , the mean number of collisions may be determined from Eq. (46), in both the vibrational [16, 17] and the rotational relaxation [18]. Such was indeed the case to find the mean numbers of collisions in experiments [19–24], where the molecules were prepared in the excited states by the method of multiphoton absorption.

4 Results and discussion

For definiteness, we are going to consider events that follow the multiphoton excitation, where a heat bath is initially cold (and remains cold), while the active molecules arise in the vibrationally excited states due to the pump laser pulse. To show actual numerical results for a concrete collisional system, we shall use parameters applicable to SF₆ in argon at 300 K [21, 25, 26]. The mean numbers of collisions are $Z_V^{ab} = 1910$ [21], $Z_V^{aa} = 108$ [25], and $P_{01}^{10} \approx 1$ [26].

Figures 1 and 2 show the distributions, calculated from Eq. (30), depending on the vibrational quantum number n for the different values of the reduced time $\nu_c t$. As

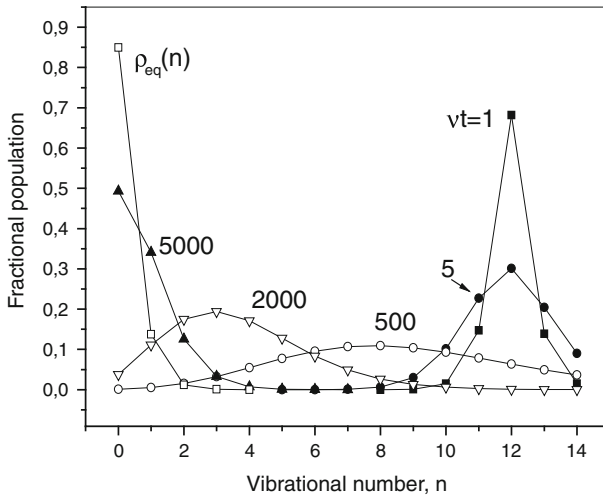


Fig. 1 The calculated fractional populations over energy levels for various numbers of collisions $v_c t$ in the system $\text{SF}_6 + \text{Ar}$ at $n' = 12$ for 1 Torr SF_6 with 100 Torr Ar

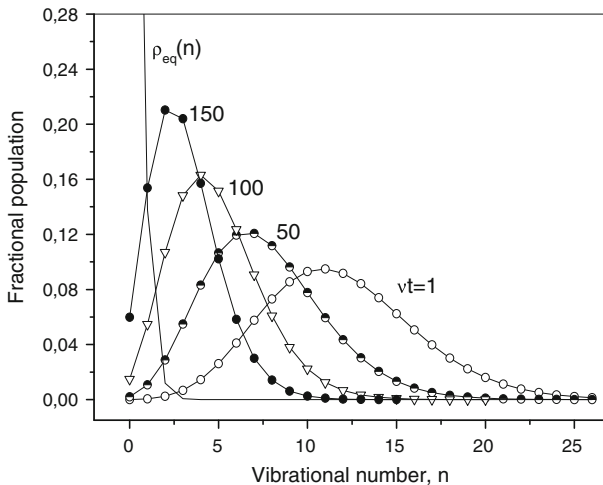


Fig. 2 The same as in Fig. 1. Pure SF_6 at 200 Torr

$v_c t$ increases, the observed peak shifts along n axis from the initial ($n' = n = 12$) to the final position, occupied by thermal distribution. Let us first analyze the case, where the excited molecules compose a small admixture in buffer gas. The initially narrow distribution strongly broadens step-by-step with a further increase in $v_c t$, but at long times it tends to a very narrow thermal distribution. This fact is interpreted as the predominant contribution of the VT-processes, where many collisions are needed ($Z_V = 1640$) to reach equilibrium (Fig. 1). In pure SF_6 , prevailing are the fast VV-processes with a characteristic time of 1 ns. The distribution becomes broad already after one collision, when all the levels are populated up to $n = 25$. Thereafter the

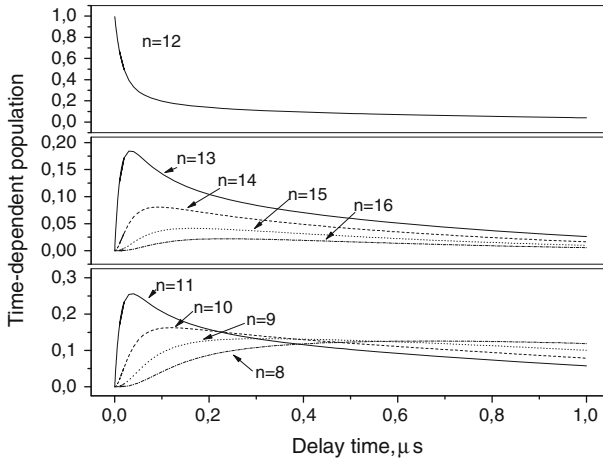


Fig. 3 Time-dependent populations for $n = 8–16$ after excitation with $n = 12$. The mixture consists of 0.1 Torr SF₆ with 100 Torr Ar. The lines show results for Eq. (30)

distribution only narrows with an increase in νt , and moves to the thermal distribution (Fig. 2).

The time-dependent populations are shown in Fig. 3. Initially, the level with $n = 12$ is excited. The population is observed to transfer at collisions from the initial to other levels. The energy transfer rates satisfy the constraint of detailed balance. Therefore, the downward transitions are preferred over the upward ones.

The absorption probability of n photons may be estimated quite readily when the absorption cross sections substantially exceed the emission ones; therefore, the induced emission is neglected [4]

$$Q_n(t) = \frac{\langle n(t) \rangle^n}{n!} e^{-\langle n(t) \rangle}, \tag{47}$$

where

$$\langle n(t) \rangle = \frac{\sigma}{h\nu} \int_0^t I(t') dt' = \langle n(\infty) \rangle \int_0^t I(t') dt' \left[\int_0^\infty I(t) dt \right]^{-1} \tag{48}$$

Here σ is the effective absorption cross section [20,24]. The mean excitation level is equal to $\langle n(t) \rangle$ for the Poisson distribution. In other words, $\langle n(t) \rangle$ is the mean number of photons absorbed per molecule in a time t . Note that $\langle n(\infty) \rangle$ is the total number of absorbed photons.

A theoretical study on the time dependence of the IR multiphoton absorption in SF₆ + Ar mixtures was performed using the microsecond pulses of the CO₂ laser as a source of excited molecules [19]. In the presence of argon gas, the number of photons absorbed per SF₆ molecule, $\langle n(t) \rangle$, are distributed between the vibrational $\langle \langle n_V(t) \rangle \rangle$ and the translational $\langle \langle n_{VT}(t) \rangle \rangle$ degrees of freedom. The decay of these quantities is

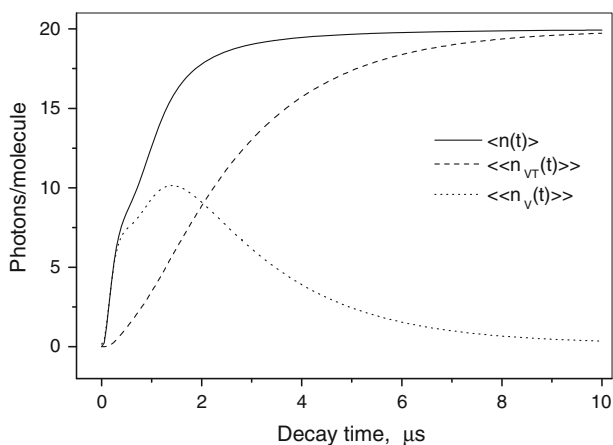


Fig. 4 The calculated vibrational energy content ($\langle \langle n_V(t) \rangle \rangle$), the number of photons transferred to the thermal bath ($\langle \langle n_{VT}(t) \rangle \rangle$), and the number of photons ($n(t)$) absorbed per SF_6 molecule against decay time. The mixture consists of 1 Torr SF_6 with 100 Torr Ar. The total number of absorbed photons is $\langle n(\infty) \rangle = 20$

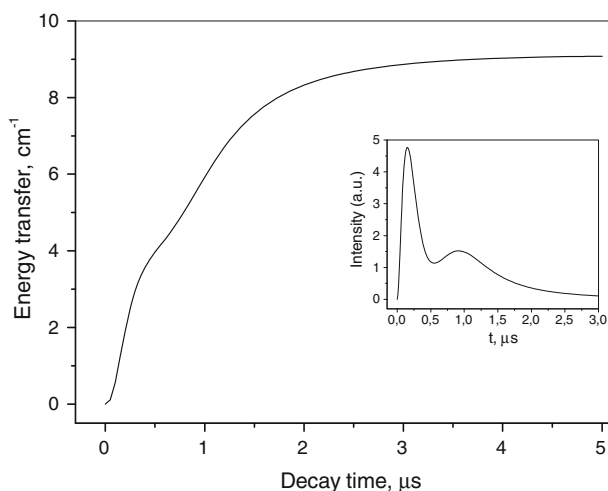


Fig. 5 The average energy transferred per collision as a function of time for 0.0002 Torr SF_6 with 1 Torr Ar. The total number of absorbed photons is $\langle n(\infty) \rangle = 19$. The inset shows the temporal profile of the CO_2 laser pulse

plotted vs. time in Fig. 4. The values were calculated from Eqs. (40), (41), and (48). The temporal profile of the CO_2 laser pulse is shown in Fig. 5.

Due to collisions, the excited molecules lose the average amount of energy ($\langle \langle \Delta E(t) \rangle \rangle$) at time t . Figure 5 presents the calculated values of the average energy transfer as a function of time. For clarity, given are the values for the time interval $0 - 5 \mu\text{s}$, though $\langle \langle \Delta E(t) \rangle \rangle$ tends to zero at long times. The maximal energy transfer is -9.0 cm^{-1} which is in fair agreement with an experimental value of -7.8 cm^{-1} [21]. As follows from Eqs. (13), (41), and (44), the average energy transfer depends

nonlinearly on the partial pressure of absorbing molecules. For example, an increase in the partial pressure of SF₆ molecules from 0.0002 Torr to 0.035 Torr in a mixture with 1 Torr of argon results in an increase in the transferred energy up to -14 cm^{-1} which is confirmed experimentally [19].

The multiphoton energy absorption from the laser field raises molecules to the highly vibrationally excited states during the short periods of time. The mean excitation level is given by the $\langle n(t) \rangle$ value. The average vibrational energy and the average transferred energy are observed to depend on the mean excitation level. For a given mixture, a maximum of the energy transfer depends mainly on the total number of photons absorbed per pulse, $\langle n(\infty) \rangle$.

The average vibrational energy is determined as the sum of $h\nu n N_n(t)$ energies over all quantum numbers. This value is given in terms of the first moment, $\langle \langle n(n', t) \rangle \rangle$, which depends only on the relaxation time $1/\varpi$ of the VT energy transfer. Thus, the collisional energy transfer depends on both the joint contribution of VT-processes and the level of excitation by laser pulses.

No energy is transferred at resonance VV-collisions. In this case, populations are redistributed over vibrational levels. These collisions are characterized by a time-scale of $1/\omega$ and produce an additional mechanism via which the molecules reach the highly vibrationally excited states.

In summary, we have shown that our phenomenological model calculations give a realistic description of the temporal evolution of populations upon collisions in the presence of multiphoton absorption for polyatomic molecules. Here we do not discuss the interesting results for SF₆ dissociation because it is beyond the scope of the present paper. Nevertheless, the basic ideas of the model seem to be fruitful for further development in this direction.

5 Appendix. The Meixner polynomials

The Meixner polynomials [27] are defined by weight function (2), where $n = 0, 1, 2, \dots$

These polynomials satisfy the orthogonality condition

$$\sum_{n=0}^{\infty} \rho_n(\theta) M_k(n, \theta) M_{k'}(n, \theta) = \delta_{kk'} \quad (49)$$

The completeness property for these polynomials is given by the expression

$$\rho_n(\theta) \sum_{k=0}^{\infty} M_k(n, \theta) M_k(n', \theta) = \delta_{nn'} \quad (50)$$

The orthonormalized Meixner polynomials are of the form

$$M_k(n, \theta) = \sqrt{g_s(k)} \exp\left(-\frac{k\theta}{2}\right) \sum_{m=0}^{m < k} \frac{1}{g_s(m)} \binom{k}{m} \binom{n}{m} (1 - e^\theta)^m, \quad (51)$$

where $m < = \min(k, n)$. Then the definition leads to the symmetry property

$$\frac{1}{\sqrt{g_s(k)}} \exp\left(\frac{k\theta}{2}\right) M_k(n, \theta) = \frac{1}{\sqrt{g_s(n)}} \exp\left(\frac{n\theta}{2}\right) M_n(k, \theta) \quad (52)$$

Relation between the Meixner polynomials and the hypergeometric function follows from the equation

$$F(-k, -n; s; z) = \sum_{m=0}^{m <} \binom{k}{m} \binom{n}{m} \frac{z^m}{g_s(m)} \quad (53)$$

The hypergeometric function of the form (53) may be expressed in terms of the Jacobi polynomials [28] to determine the relation between the Meixner and Jacobi polynomials

$$M_k(n, \theta) = \frac{1}{\sqrt{g_s(k)}} \exp\left(\frac{k\theta}{2}\right) P_k^{(s-1, n-k)}(2e^{-\theta} - 1) \quad (54)$$

There is an abundant literature where the useful formulas are given for the Jacobi polynomials [27–29]. In particular, the generating function of Jacobi polynomials is of the form [29]

$$\sum_{k=0}^{\infty} t^k P_k^{(s-1, n-k)}(2e^{-\theta} - 1) = \frac{(1-t)^n}{(1-te^{-\theta})^{n+s}}, \quad t < 1 \quad (55)$$

This equation may be used to derive a generating function for the Meixner polynomials which is convenient to rewrite as

$$\sum_{k=0}^{\infty} e^{-k\alpha} \sqrt{g_s(k)} M_k(n, \beta) = \frac{1}{(1-e^{-\alpha-\beta/2})^s} \left(\frac{1-e^{-\alpha+\beta/2}}{1-e^{-\alpha-\beta/2}} \right)^n \quad (56)$$

The symmetry property (54) allows one to write this relation in a different form

$$\sum_{n=0}^{\infty} e^{-n\alpha} g_s(n) M_k(n, \beta) = \frac{\sqrt{g_s(k)} e^{-k\beta/2}}{(1-e^{-\alpha})^s} \left(\frac{1-e^{-\alpha+\beta}}{1-e^{-\alpha}} \right)^k \quad (57)$$

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