Singularities of collisional vibrational relaxation processes in strongly excited spectrally complex polyatomic molecules

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Singularities are considered of collisional processes that take place in complex polyatomic molecules under condition when the vibration-stochastization time is much shorter than the characteristic time of molecule interaction with one another in collisions. It is shown that collisions between stochastic molecules and buffer gas molecules, a process in which significant energy transfer is impossible, lead to diffusion of the population over the energy spectrum. The population distribution function that results from the elementary collision act is obtained, as well as the coefficient of diffusion of the population in energy space. Expressions are derived for the change of the population distribution function in collisions of two identical stochastic molecules. Using an analytically solvable model problem as an example, it is shown that the *V–V* exchange process in strongly excited stochastic molecules is not diffusive. The time of relaxation of the population-energy distribution function to its stationary (thermal) form is estimated. The singularities of vibrational-excitation transfer to isotopically substituted molecules are discussed.

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§1. INTRODUCTION

The investigation of collisionless dissociation of polyatomic molecules[1] is the subject of many studies, reviews,[2–7] and monographs.[8,9] So far, however, there is no unified treatment of this phenomenon, combining a consistent theoretical approach that leads to numerical results with an analysis of the experimental observation. The reason is not only that the phenomenon itself is too complicated to analyze theoretically and calls for the study of the stochastic vibrational dynamics of a multimode molecule, but also that an appreciable part of the experimental results was obtained under conditions when the process of energy accumulation in a laser field is influenced by rapid vibrational exchange of excitation between the molecules via collisions.[10]

The influence of intermolecular exchange of vibrational excitation in collisions (*V–V* exchange)[11,12] on the dynamics of molecule excitation in a laser field was investigated in detail by Platonenko and Sukhareva[13] within the framework of a model of coherent interaction of oscillators, when the main contribution to the collision dynamics is made by frequent collisions during which the level populations change little. This model works well in the description of *V–V* exchange at low levels of polyatomic molecules. To describe collision dynamics of the populations of high levels under conditions when the internal vibrational motion of the molecule is essentially stochastic, and the characteristic correlation-loss time τ_c (estimated as the reciprocal width of the absorption contour) is much shorter than the time τ_i of the interaction of the molecules in the course of the collision, substantial modification of the cohterent-interaction model is necessary.

The purpose of the present paper is to describe the collision of molecules within the framework of the model of completely uncorrelated matrix elements of the interaction operator,[14] a model corresponding to the case of rapid (compared with the characteristic time of the change of the level population in the course of the collisions) stochastization of the vibrations ($\tau_c \ll \tau_i$). The molecule collisions are described in the following sequence. We consider first the elementary act of collision of a molecule with a buffer gas, when there is actually no energy exchange between the molecules in the collision because the process is nonresonant, and discuss the kinetic consequences of this effect. This is followed by investigation of the elementary act of collision of two identical molecules, at least one of which is in a highly excited state. Finally, an equation is derived for the paired distribution function, from which a kinetic equation is obtained for the single-particle distribution function in a simple example that lends itself to an analytic treament. For a single-particle distribution function, model equations that describe the transfer of vibrational excitation from the molecule of one isotope to a molecule of another isotope will also be given.

It must be noted that the collision can change not only the energy of each of the colliding molecules, but also the population distributions, in phase space, of their internal variables. This situation is most probable in the case of a collision between an excited molecule and a buffer-gas molecule, when the interaction that plays the principal role is not dipole-dipole and is not characterized by any selection rule whatever. This phenomenon is not discussed in the present paper. We assume that the *V–V* exchange due to the dipole-dipole interaction does not alter the phase–space population distribution function obtained by laser excitation, and the elementary collision act with the buffer gas molecules produces, on the contrary, a uniform population of all of phase space. It is assumed here, in addition, that the main contribution to the collisional redistribution of the level populations is due to collisions with practically no change of the translational motion of the molecules.

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§2. ELEMENTARY ACT OF COLLISION OF AN EXCITED MOLECULE WITH A BUFFER-GAS MOLECULE

We assume that a molecule on a high excitation level has an energy spectrum E_n, where n numbers the quantum level. A buffer-gas molecule aproaching the molecule in question produces between the levels an additional interaction described by an increment $G(R)V_{nn'}$ to the Hamiltonian, where $G(R)$ is a function of the time-variable distance between the molecule, and the matrix $\hat{V}$ has a complicated structure by virtue of the assmption made that the internal vibrational motion of the molecule is stochastic.[14] The energy of the interaction between the vibrational levels of the considered molecule is much lower than thermal, so that the relative motion of the colliding molecules can be regarded as given, i.e., $R=R(t)$ and $G=G(t)$. In this case the ψ functions of the vibrational states of the considered molecule satisfy the Schrödinger equation ($\hbar\equiv 1$):

$$
\begin{aligned}
&i\dot{\psi}_n=E_n\psi_n+V_{nn'}G(t)\psi_{n'},\\
&-i\dot{\psi}_n^*=E_n\psi_n^*+V_{nn'}^*G(t)\psi_{n'}^*.
\end{aligned}
\tag{1}
$$

For convenience in the derivation of the equations that describe the dynamics of the populations, we assume that the function $G(t)$ is periodic and has a discrete spectrum:

$$
G(t)=\sum_k G_k e^{ik\Omega t},
\tag{2}
$$

with $G_k=-G_{-k}$, i.e., $G|_{t=0}=0$. It will be clear from the answer that this assumption is not a stringent requirement, and that the result can be generalized to include the case of a function $G(t)$ that varies smoothly from $-\infty$ to $+\infty$.

We seek the solution of Eqs. (1) in the form

$$
\psi_n=\sum_m \psi_{n,m}(t)e^{im\Omega t},\quad \psi_n^*=\sum_m \psi_{n,m}^*(t)e^{im\Omega t}.
\tag{3}
$$

In this case each of the harmonics $\psi_{n,m}(t)$ satisfies the equations

$$
\begin{aligned}
&i\dot{\psi}_{n,m}-m\Omega\psi_{n,m}=E_n\psi_{n,m}+V_{n,n'}G_{m-m'}\psi_{n',m'},\\
&-i\dot{\psi}_{n,m}^*-m\Omega\psi_{n,m}^*=E_n\psi_{n,m}^*+V_{n,n'}G_{m'-m}\psi_{n',m'}^*.
\end{aligned}
\tag{4}
$$

We take the Fourier transform

$$
\psi_{n,m}(t)\rightarrow\psi_{n,m}(\varepsilon),\quad \psi_{n,m}^*(t)\rightarrow\psi_{n,m}(-\xi),
$$

introduce the matrix

$$
\rho_{n,m}^{n',m'}(\varepsilon,\xi)=\psi_{n,m}(\varepsilon)\psi_{n',m'}(\xi)
\tag{5}
$$

and represent it in the form of a series in powers of $\hat{\bar{V}}$. We use the assumption that the matrix V has a complicated structure and use also the ensemble-averaging procedure,[14–16] introducing also the operators

$$
\begin{aligned}
&\hat{X}_n=(\hat{I}\varepsilon-E_n\hat{I}-\Omega\hat{B}+i\langle V^2\rangle\pi g(E)\hat{G}\hat{G})^{-1},\\
&\hat{\bar{X}}_n=(\hat{\bar{I}}\xi-E_n\hat{\bar{I}}-\Omega\hat{\bar{B}}-i\langle V^2\rangle\pi g(E)\hat{G}\hat{G})^{-1},
\end{aligned}
\tag{6}
$$

where the matrices that enter in the expression have the following matrix elements:

$$
\begin{aligned}
&\langle m|\hat{I}|m'\rangle=\langle m|\hat{\bar{I}}|m'\rangle=\delta_{m,m'},\\
&\langle m|\hat{B}|m'\rangle=\langle m|\hat{\bar{B}}|m'\rangle=m\delta_{mm'},\\
&\langle m|\hat{G}|m'\rangle=G_{m-m'},\quad \langle m|\hat{\bar{G}}|m'\rangle=G_{m'-m}
\end{aligned}
\tag{7}
$$

(the operators with the superior bar act on $\psi(\xi)$ or on the upper indices, and the operators without the bar on $\psi(\varepsilon)$ or on the lower indices of the density matrix $\rho_{n,m}^{n',m'}$. After summing the series, the expression for the density matrix takes the form

$$
\begin{aligned}
\hat{\rho}_n{}^n={}&\hat{X}_n\hat{\bar{X}}_n\langle V^2\rangle\hat{G}\hat{\bar{G}}\{(\varepsilon-\xi)\hat{I}\hat{\bar{I}}-\Omega(\hat{B}\hat{\bar{I}}-\hat{\bar{B}}\hat{I})\\
&+\pi ig\langle V^2\rangle(\hat{G}\hat{G}\hat{\bar{I}}\\
&+\hat{I}\hat{\bar{G}}\hat{\bar{G}})-2\pi ig\langle V^2\rangle\hat{G}\hat{\bar{G}}\}^{-1}\hat{X}_r\hat{\bar{X}}_r\hat{\rho}_r{}^r|_{t=0}+\hat{X}_n\hat{\bar{X}}_n\hat{\rho}_n{}^n|_{t=0},\\
g(E)\equiv{}&g.
\end{aligned}
\tag{8}
$$

The Fourier transformation with respect to the lower and upper indices can reduce the equations for the matrices $\hat{X}_n$ and $\hat{X}_n$ as well as for the matrix

$$
\hat{Z}=(\hat{\bar{X}}_n\hat{X}_n)^{-1}(\hat{X}_0\hat{\bar{I}}-\hat{I}\hat{\bar{X}}_0)
\tag{9}
$$

to equations that can be solved in quadratures

$$
\begin{aligned}
&\left(\varepsilon-E_n+i\frac{\partial}{\partial\tau}\right)X(\tau,\tau')+i\pi g\langle V^2\rangle G^2(\tau)X(\tau,\tau')=\delta(\tau-\tau'),\\
&\left(\xi-E_n-i\frac{\partial}{\partial\theta}\right)\bar{X}(\theta,\theta')-i\pi g\langle V^2\rangle G^2(\theta)\bar{X}(\theta,\theta')=\delta(\theta-\theta'),\\
&\left(\varepsilon-\xi+i\frac{\partial}{\partial\tau}+i\frac{\partial}{\partial\theta}\right)Z(\tau,\tau',\theta,\theta')\\
&\qquad+i\pi g\langle V^2\rangle(G(\tau)-G(\theta))^2Z(\tau,\tau',\theta,\theta')\\
&\qquad=\delta(\tau-\tau')\delta(\theta-\theta'),
\end{aligned}
\tag{10}
$$

Taking the inverse Fourier transform with respect to time we find that the population of a level separated from the initial populated level by a distance δ is given by

$$
\begin{aligned}
\rho(E_0+\delta;t)={}&\mathrm{Re}\int_0^t e^{i\delta\vartheta}\exp\Big\{-2\pi g\langle V^2\rangle\\
&\times\Big[\int_0^t G^2(\tau)d\tau-\int_\vartheta^{t-\vartheta}G(\tau)G(\tau+\vartheta)d\tau\Big]\Big\}d\vartheta.
\end{aligned}
\tag{11}
$$

The generalization of (11) to include the case of an interaction intensity that varies smoothly from $t=-\infty$ *to* $t=+\infty$ is of the form

$$
\begin{aligned}
\rho(\delta)|_{t=\infty}={}&\mathrm{Re}\int e^{i\delta\tau}\exp\Big\{-2\pi g\langle V^2\rangle\int_{-\infty}^{\infty}[G^2(t)\\
&-G(t)G(t+\tau)]dt\Big\}d\tau.
\end{aligned}
\tag{12}
$$

In other words, the population distribution resulting from the elementary collision act is equal to the Fourier transform of the exponential of the correlation function of the interaction energy.

Expression (12) makes it possible to determine the coefficient of the population diffusion in energy space

$$
\begin{aligned}
D={}&\int w_{\mathrm{col}}(GV)dV\int_{-\infty}^{\infty}\delta^2d\delta\,\mathrm{Re}\int\exp\Big\{i\delta\tau-2\pi g\langle V^2\rangle\int_{-\infty}^{\infty}[G^2(t)\\
&-G(t)G(t+\tau)]dt\Big\}d\tau\\
={}&\int w_{\mathrm{col}}(GV)2\pi g\langle V^2\rangle\int_{-\infty}^{\infty}G(t)\ddot{G}(t)\,dt\,dV,
\end{aligned}
\tag{13}
$$

where $w_{\rm col}(GV)$ is the probability of collision with an interaction amplitude GV.

Estimates based on Eq. (13) using the additional assumption that the characteristic energy of the vibrational interaction at characteristic atomic distances is estimated as the product of the square of the product of the squared Born-Oppenheimer parameter by the characteristic thermal energy, show that the time of equilization of the population over the entire spectrum amounts to $\tau = 10^{-1}$–10^{-2} sec·Torr. Thus, the elementary act of collision of the molecule with a buffer-gas molecule leads to broadening of the energy distribution of the population and can ensure establishment of an equilibrium distribution only over times on the order of 10^{-1}–10^{-2} sec·Torr.

§3. ELEMENTARY ACT OF HIGHLY-EXCITED-MOLECULE COLLISION ACCOMPANIED BY VIBRATIONAL-ENERGY TRANSFER

The interaction energy of two colliding molecules can be expressed as an expansion in powers of normal coordinates. The resonant vibrational exchange is represented in this expansion by quadratic forms in the normal coordinates of each of the modes. In collisions of molecules with impact parameters that exceed the characteristic geometric dimensions of the molecules, a substantial contribution is made by dipole-active modes, for only they correspond to expansion coefficients that decrease non-exponentially with increasing impact parameter. At such distances it suffices to consider only IR-active modes that interact via the dipole-dipole mechanism.

The collision of two polyatomic molecules having IR-active modes can be described within the framework of the band theory of spectra.[17,18] Each molecule has a self-energy function ψ_n and $\psi_{m\beta}$, where the first index numbers the band and the second the level in this band. A system of two molecules is described b a four-index function $\psi_{n,m,\alpha\beta}$. The eight-index matrix $\hat V$

$$\hat V = -R^{-5}(t)\,[3(\hat{\mathbf d}_1,\ \mathbf R(t))\,(\hat{\mathbf d}_2,\ \mathbf R(t)) - (\hat{\mathbf d}_1,\ \hat{\mathbf d}_2)R^2(t)] \quad (14)$$

which depends on the time and has a complicated structure, corresponds to the dipole-dipole interaction operator.[19] We note that, as follows from the results of Ref. 16, when the characteristic time τ_i of the interaction is much longer than the characteristic stochastization time but is much shorter than the characteristic reciprocal distance between the neighboring levels of the spectrum of a system of two molecules, the equation for the populations can be derived under the assumption that V does not depend on t. The time dependence can be taken into account then in the final expressions for the populations.

We introduce the notation

$$N={}^1/_2(n+m),\ M={}^1/_2(n-m),\ \Delta_{N,\,M,\,\alpha,\,\beta}=E_{n,\,\alpha}+E_{m,\,\beta},$$

$$V_{n,m,\alpha,\beta}^{n+1,m-1,\alpha',\beta'}=V_{N,M,\alpha,\beta}^{N,M+1,\alpha',\beta'},\qquad V_{n,m,\alpha,\beta}^{n-1,m+1,\alpha',\beta'}=V_{N,M,\alpha,\beta}^{N,M-1,\alpha',\beta'},$$

where $E_{n\alpha}$ and $E_{m\beta}$ are the energies of the first and second molecules. In this notation Eq. (14) takes the form

$$i\dot\psi_{N,M,\alpha,\beta}=\Delta_{N,M,\alpha,\beta}\psi_{N,M,\alpha,\beta}$$
$$+V_{N,M,\alpha,\beta}^{N,M+1,\alpha',\beta'}\psi_{N,M+1,\alpha',\beta'}+V_{N,M,\alpha,\beta}^{N,M-1,\alpha',\beta'}\psi_{N,M-1,\alpha',\beta'}. \quad (15)$$

Equation (15) coincides formally with the equation that describes the dynamics of the excitation of a multilevel system of the band type in a laser field.[14] The main difference is that the band levels (the bands are labeled by the index M) are numbered not by one but by two (Greek) indices. Performing the same operations as in Ref. 14 (Fourier transformation, with respect to time, of Eq. (15) and of the analogous equation for the complex-conjugates, representation of the solution of these equation by a series in powers of the operator $\hat V$, term-by-term multiplication of the series, and selection of the terms in which each matrix element of the operator $\hat V$ is encountered an even number of times, spectrum renormalization that leads to the appearance of imaginary additions to the energy eigenvalues, and summation of the series for the population), we find that the total energy of the interacting molecules deviates little from its initial value, and the dynamics of the level populations of the two molecules is described by the following kinetic equation:

$$\dot\rho_{N,M}(\delta)=\int d\delta'[-D_{N,M+1}^{N,M}(t,\delta,\delta')\rho_{N,M}(\delta)$$
$$-D_{N,M-1}^{N,M}(t,\delta,\delta')\rho_{N,M}(\delta)$$
$$+D_{N,M}^{N,M-1}(t,\delta,\delta')\rho_{N,M-1}(\delta')+D_{N,M}^{N,M+1}(t,\delta,\delta')\rho_{N,M+1}(\delta')], \quad (16)$$

where $\delta = E_{n,\alpha} - E_{n,\beta} - n\omega + m\omega$, and the kinetic coefficient is

$$D_{N,M}^{N,M'}(t,\delta,\delta')$$
$$=\frac{12\pi}{R^6(t)}g(N\omega+M\omega+\Delta+\delta')\,g(N\omega-M\omega+\Delta-\delta')$$
$$\times\langle d^2(N\omega+M\omega+\Delta+\delta;\ N\omega+M'\omega+\Delta-\delta')\rangle$$
$$\times\langle d^2(N\omega-M\omega+\Delta-\delta;\ N\omega-M'\omega+\Delta-\delta')\rangle. \quad (17)$$

Here $\langle d^2(a;b)\rangle$ is the mean squared matrix element of the dipole-moment operator for transitions from molecule levels lying in the vicinity of the energy a to levels in the vicinity of the energy b, and $\Delta = \Delta_{n,\alpha} + \Delta_{m,\beta}$. The population is then localized in a narrow vicinity of the two-molecule energy-space layer corresponding to the initial energy.

The kinetic equation (16) with the kinetic coefficients (17) has a lucid physical meaning. During the time of flight of one excited molecule relative to the other, photon exchange can take place between them, accompanied by a change in the distribution of the populations of the molecules. One of the molecules, located, say, in band n on a level shifted by an amount $\Delta_{n,\alpha}$ from the resonant value of the energy, can emit a photon of frequency $\omega + \delta$ with a spectral probability density

$$g(n\omega-\omega+\Delta_{n,\,\alpha}-\delta)\,\langle d^2(n\omega+\Delta_{n,\,\alpha};\ n\omega-\omega+\Delta_{n,\,\alpha}-\delta)\rangle$$

and consequently produce around itself radiation at a frequency $\omega + \delta$ with a spectral intensity

$$I\infty E^2=6R^{-6}(t)\,[g(n\omega-\omega+\Delta_{n,\,\alpha}-\delta)$$
$$\langle d^2(n\omega+\Delta_{n,\,\alpha};\ n\omega-\omega+\Delta_{n,\,\alpha}-\delta)\rangle]. \quad (18)$$

The other molecule, located in band m at a level with a deviation $\Delta_{m,\beta}$ in such a field, can absorb the emitted photon with a probability

$$2\pi E^2\langle d^2(\omega m+\Delta_{m,\,\beta};\ \omega m+\omega+\Delta_{m,\,\beta}+\delta)\rangle g(\omega m+\omega+\Delta_{m,\,\beta}+\delta). \quad (19)$$

Substitution of (18) in (19), with allowance for the performed change of variables, leads to expression (17).

It must be noted that the elementary collision process that takes place with a small value of the impact parameter has a high probability of being accompanied by exchange of not only one but also many photons. The reason is that with decreasing impact parameter the characteristic number of photons transferred from one molecule to the other increases more rapidly than the decrease of he probability of collision at this value of the impact parameter.

If the relative velocity of the molecules is v and the impact parameter is r, the collision results in a state-population change given by

$$\rho_{n,m,\alpha,\beta}=\sum_{n',m',\alpha',\beta'}\left\langle n,m,\alpha,\beta\left|\exp\int_{-\infty}^{\infty}\hat{K}(R)\,dt\right|n',m',\alpha',\beta'\right\rangle \times\rho_{n',m',\alpha',\beta'}\big|_{t=-\infty},$$

$$R=[r^2+v^2t^2]^{1/2},\tag{20}$$

where $\hat{K}(R)$ is the integro-difference operator in the right-hand side of (16).

Thus, the elementary act of collision of two identical strongly excited molecules, between which dipole-dipole interaction can produce vibrational exchange, results in diffusion of the population over the band spectrum of each of the molecules and over the vibrational states within each band. The diffusion takes place in steps corresponding to exchange of photons of definite frequency, as a result of which the molecules go over to neighboring (one to the upper, the other to the lower) bands into states that are separated from the harmonic value of the energy by an amount determined by the form of the frequency characteristic of the absorption and emission of the photons. The probability of each diffusion step depends on the numbers of the bands of each of the molecules (i.e., on their energies) and on the positions of the levels in the band, and is determined by the product of the probabilities of emitting and absorbing photons of a definite frequency, or in other words by the frequency characteristic of the probability of radiation absorption by the quasicontinuum levels. The number of diffusion steps is determined by the values of the relative velocity of the molecules and of the impact distance. The summary effect of the collision is given by Eq. (20).

§4. KINETIC EQUATIONS FOR THE MOLECULE DISTRIBUTION FUNCTION IN ENERGY SPACE

Starting from the results of the preceding section, we can write down equations for the paired distribution function of the populations:

$$\rho_{n,m}(\Delta_1,\Delta_2)=\sum_{n',m'}\int d\Delta_1'\,d\Delta_2'\,dv\,dr\,w(v,r)\,[S_{n,m}^{n',m'}(v,r,\Delta_1,\Delta_2,\Delta_1',\Delta_2')\times\rho_{n',m'}(\Delta_1',\Delta_2')-\rho_{n,m}(\Delta_1,\Delta_2)S_{n,m}^{n',m'}(v,r,\Delta_1,\Delta_2,\Delta_1',\Delta_2')],\tag{21}$$

where

$$\hat{S}=\exp\int_{-\infty}^{\infty}\hat{K}(R)\,dt,\tag{22}$$

and $w(v,r)$ is the probability of molecule collision with relative velocity v and impact parameter r. The first term of the expression in the square brackets in (21) describes the influx into the state $(n;\Delta_1;m;\Delta_2)$ while the second term describes the outflow from this state. It must be noted that by virtue of the assumption that the translational motion of the molecules does not change during the vibrational exchange, we get the relation

$$\sum_{m',n'}\int d\Delta_1'\,d\Delta_2'S_{n,m}^{n',m'}(v,r,\Delta_1,\Delta_2,\Delta_1',\Delta_2')=1.\tag{23}$$

For further calculations we need detailed information on the values of the kinetic coefficients of the transitions between the states of the band spectrum of the molecules under the action of the radiation. If these values are known, a numerical calculation allows us to construct the matrix $\hat{S}$ and to proceed to solve (21) numerically. In all probability, however, it is premature to undertake such a laborious program in its entirety, for we are still far from a compelte solution of the problem of obtaining the kinetic coefficients, their spectral dependences, and the mechanisms by which they are formed, despite the large number of papers on this subject.[20–25]

It seems advisable to investigate analytically a simplified model problem with the aim of obtaining the basic characteristic regularities of a collision between highly excited molecules; this can facilitate considerably the development of satisfactory phenomenological models. As the simplest, we choose a model in which the kinetic coefficients $D_{n,m}^{n',m'}$ at $n+m=n'+m'$ and $n-m=n'-m'\pm 2$ do not depend on the degree of excitation of the molecules n and m, and we ignore the diffusion over the band levels, assuming that it does not alter substantially the effective averaged kinetic coefficients of the band-to-band transitions. The following expression is then valid for the matrix $\hat{K}$:

$$K_{n,m}^{n',m'}=\frac{12\pi d^4}{(r^2+v^2t^2)^3\beta}\delta_{n+m}^{n'+m'}(\delta_n^{n'+1}\delta_m^{m'-1}+\delta_n^{n'-1}\delta_m^{m'+1}-2\delta_n{}^{n'}\delta_m{}^{m'}),\tag{24}$$

where d is the characteristic dipole moment of the 0–1 transition, and β is the characteristic value of the anharmonicity constant. Using an integral representation for the function of an operator[26] in the expression for the matrix inverse to $(z-K_{n,m}^{n',m'})$ in terms of Chebyshev polynomials, integrating with respect to time, using a Maxwellian distribution for the relative velocity, and integrating over the impact parameters, we obtain

$$\dot{\rho}_{n,m}=-\frac{\pi}{5}\Gamma\left(\frac{4}{5}\right)\left(\frac{36\pi^2d^4}{4\beta}\right)^{2/5}v_T^{3/5}n_0\int_0^{\infty}u^{-7/5}(e^{-u}-1)\,du \times\sum_{n',m'}\delta_{n+m}^{n'+m'}\frac{1}{2\pi i}\int_C(1-\cos\pi\theta)^{2/5}\cos[(n-1/2)\pi\theta] \times\cos[(n'-1/2)\pi\theta]\operatorname{ctg}[(n'+m')\pi\theta]\,d\theta\,\rho_{n',m'},\tag{25}$$

where v_T is the characteristic thermal velocity, n_0 is the particle density, and the integration contour C encloses the segment (0,2).

Equation (25), which describes the dynamics of the paired distribution function, has a stationary solution

$$\rho_{n,m}=Fe^{-\lambda(n+m)}, \tag{26}$$

where F is a normalization factor. Expression (26) is in fact a thermal distribution, the only difference being that by virtue of the model assumptions (24) no account is taken of the statistical weight of the states. From (25) and (26) one can obtain for the single-particle distribution function $\tilde{\rho}_n$ a kinetic equation that differs little from the thermal one:

$$\rho_n=(n_0-\tilde{n}_0)e^{-\lambda n}(e^{\lambda}-1)^{-1}+\tilde{\rho}_n, \tag{27}$$

where $\tilde{n}_0$ is the density of the nonthermal molecules. Assuming a parameter $\lambda \ll 1$ and a characteristic value $n \gg 1$, meaning a strong suprathermal excitation of the nonthermal molecules, changing from the discrete variables n to the continuous x, and assuming that $\tilde{\rho}(x)|_{x=n}=\rho_n$ is a smooth function, i.e., $\partial\tilde{\rho}/\partial x \ll \tilde{\rho}$, we obtain for this function the equation

$$\rho(x)=-(A-2D)\rho(x)+D\frac{\partial^2}{\partial x^2}\rho(x)$$
$$+(A-2D)f(x)-D\frac{\partial^2}{\partial x^2}f(x), \tag{28}$$

where $f(x)$ is the stationary distribution function $F\exp(-\lambda x)$ normalized to the density of the nonthermal molecules, while A and D satisfy the relations

$$A=C\Gamma\left(\frac{24}{5}\right)\frac{2}{\pi}\cos\left(\frac{12\pi}{5}\right)\int_0^1 u^{7/5}(1+u)^{-24/5}\,du,$$
$$D=C\Gamma\left(\frac{24}{5}\right)\frac{2}{\pi}\cos\left(\frac{12\pi}{5}\right)\int_0^1 u^{9/5}(1+u)^{-24/5}\,du, \tag{29}$$
$$C=-\frac{\pi}{5}\Gamma\left(\frac{4}{5}\right)\left(\frac{9\pi^2d^4}{\beta}\right)^{2/5}v_T^{3/5}n_0\int_0^\infty u^{-7/5}(e^{-u}-1)\,du.$$

It can be seen from (28) that the distribution function that differs little from thermal relaxes to its stationary (thermal) form exponentially at a characteristic rate A, and that a kinetic equation in the τ-approximation[28,29] corresponds best to the described process. This is the main difference between the case of collision of highly excited molecules and the collision of weakly excited or nonstochastic molecules,[13] where the approach of the distribution function to its stationary form obeys the diffusion law. The reason for this is the following: owing to the rapid stochastic motion, the probability of transferring a photon from one molecule to another is inversely proportional to the sixth power of the intermolecular distance (and not to the cube as in the case of coherent interaction), therefore the total number of photons transferred during the entire time of the elementary collision act is inversely proportional to the fifth power of the impact parameter (and not to the square). Accordingly, the main contribution to the collision integral is made by small values of the impact parameter and by large values of the energy transfer. In othe words, the collision typical of highly excited complex polyatomic molecules is one during which the molecule populations are practically equalized. If the fraction of nonthermal molecules is small and the collisions are mainly with thermal molecules, this means in fact an exponential decrease of the distribution function to its stationary value.

It must be emphasized that owing to the decisive contribution of the collisions with large energy transfer, the equations obtained do not contain a dependence of the excitation-relaxation rate on the reverse of the vibrational energy in the strongly-excited-molecule fraction. Indeed, the ratio of the probability of transferring n photons and $10n$ photons is only 1.7, so that the characteristic relaxation time of strongly excited stochastic molecules differs little from the relaxation time of weakly excited stochastic molecules. This difference is taken into account by the kinetic-equation term that contains the second derivatives. In addition, by virtue of the model assumptions made, such a relaxation-time ratio is obtained without account of the fact that in the elementary collision act the probability of one diffusion step can be substantially larger for strongly excited molecules than for weakly excited ones. Allowance for this circumstance should lead to an even smaller difference between the relaxation rates.

Let us estimate the population relaxation rate. At $v_T = 1.29\times10^5$ cm/sec, $d=1$ D, $\beta=1$ cm^{-1}, and $n_0=3.5\times10^{16}$ cm^{-3} the value of A is 5.5×10^{-8} sec·Torr; at $d=0.6$ D we have $A=8.3\times10^{-8}$ sec·Torr. The characteristic impact parameters are in this case $\frac{1}{2}(9\pi^2d^4/\hbar\beta v)^{1/5}\approx 30-40$ Å, much larger than the characteristic geometric dimensions of the molecules.

Equations that describe the transfer of vibrational excitation from one isotopic component of a molecular gas to another can be obtained in similar fashion. We can use for this purpose a model similar to (24), in which account must be taken of the isotope frequency shift and the long-wave shift of the contour of photon absorption and emission as the molecules are excited.[29] Under these conditions, excitation exchange between molecules of different isotopes can occur only if the molecule of the lighter isotope is excited above a definite limit $x>k$, when the shift of its spectral characteristics can be offset by the isotope shift of the frequency, and the photons in its emission spectrum have frequencies that are at resonance with the frequencies of the main transition of the molecule of the heavier isotope.

The equations that model this process, without allowance for the terms that describe the diffusion of the populations, are

$$\begin{aligned}\dot{\tilde{\rho}}_1(x)&=-A[\tilde{\rho}_1(x)-f_{1\,\text{ст}}(x)]\\&\quad+A'[\tilde{\rho}_2(x+1-k)-f_{2\,\text{ст}}(x+1-k)],\\\dot{\tilde{\rho}}_2(x)&=-A[\tilde{\rho}_2(x)-f_{2\,\text{ст}}(x)]\\&\quad+A'[\tilde{\rho}_1(x+1+k)-f_{1\,\text{ст}}(x+1+k)],\end{aligned} \tag{30}$$

where $\tilde{\rho}_1(x)$ and $\tilde{\rho}_2(x)$ are the distribution functions of the nonthermal molecules of the heavier and lighter isotopes, respectively. Equations (30), just as (28), have terms that describe the relaxation of the distribution functions of the molecules of each of the isotopes to their stationary (thermal) form on account of the collisions with thermal molecules similar to them. In addition, however, there are crossover additions that describe the transfer of above-threshold excitation of the molecules of the lighter isotope to those of the heavier.

For a rigorous description of the exchange of vibrational energy between molecules of different isotopes we must, of course, know the exact spectral characteristic and solve numerically the kinetic equations. In a model description with the aid of Eqs. (30) it suffices to estimate the ratio of the constants A and A'. The roughest estimate of these quantities can be based on the form of the frequency dependence of the absorption coefficient. If it is assmed that the nonthermal molecules are excited by laser radiation to energies equal on the average to half the dissociation energy, the ratio of the constants A and A' is given by

$$A'/A=\sigma(E=U_D/2;\ \omega_2)/\sigma(E=U_D/2;\ \omega_1), \qquad (31)$$

where $\sigma(E=U_D/2;\omega)$ is the frequency dependence of the cross section for radiation absorption by the lighter-isotope molecule excited to an energy equal to half the dissociation energy ω_2 is the frequency of the main transition of the molecule of the heavier isotope, and ω_1 that of the lighter isotope. For the SF_6 molecule this ratio is approximately 3.5, i.e., the rate of excitation transfer from $^{32}SF_6$ to $^{34}SF_6$ is of the order of 2×10^{-8} sec·Torr (if it is assumed that $\beta=1\ \text{cm}^{-1}$ and $d=1$ D).

Thus, in a mixture of molecules of different isotopes, in which a red shift takes place in the radiation-absorption characteristic with increasing vibrational excitation, the collisional relaxation proceeds in two stages under conditions of strong superthermal excitation of a small fraction of molecules of the lighter isotope. First the fraction of molecules excited above the threshold for excitation transfer between isotopes transfers rapidly its energy in excess of this threshold to the molecules of the heavier isotopes, and then a dominant role is assumed by the relaxation of the distribution functions of each of the isotoes to its stationary (thermal) form.

§5. CONCLUSIONS

1. When a complex excited molecule collides with a buffer-gas molecule, the population diffuses in energy space. As a result of the elementary collision act the population initially localized on one level of the complex vibrational spectrum of the molecule is distributed among the levels closest in energy. The population distribution function as a function of the energy deviation is in this case the Fourier transform of an exponential of the correlation function of the interaction energy. After times on the order of 10^{-1}–10^{-2} sec·Torr the multiple collisions cause smearing of distribution function by an amount of the order of the energy of the laser quantum.

2. The elementary act of collision of two identical polyatomic molecules, at least one of which is in a highly excited state, is a multiple incoherent photon-exchange process. This process is described by a kinetic equation and constitutes diffusion in the space of the number of quanta of each of the molecules and in the space of the deviations of the energy levels from the harmonic position at a fixed total energy of the molecules. The kinetic coefficient and the matrix that describes the summary effect of the change of the populations in the elementary collision act are determined by integrals of the spectral probabilities of the photon emission and absorption, multiplied by a function of the impact distance and of the relative velocity of the molecules.

3. The character of the dynamics of the single-particle energy distribution function of highly excited molecules is determined mainly by the infrequent collisions with small values of the impact distance, as a result of which a large number of vibrational quanta is exchanged. It is best to use the τ-approximation for the kinetic equation that describes the single-particle distribution function of the colliding polyatomic molecules that are in stochastic states. After a characteristic time τ estimated as corresponding to 55×10^{-9} sec·Torr the distribution function relaxes exponentially to its stationary (thermal) form.

4. Energy transfer from highly excited molecules of a light isotope to unexcited molecules of a heavy isotope can be several times faster than the collisional relaxation if the contour of the radiation absorption by the molecules is red-shifted with increasing vibrational excitation. The reason is that an excited molecule of the light isotope emits with higher probability low frequency photons that are resonant to the main transition of the molecule of the heavy isotope, than the high frequency photons resonant to the main transition of the molecule of the light isotope.

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