# On some macroscopic quantum effects in low-density molecular gases

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Examples of the collisional stimulation of the intramolecular motions in polyatomic molecules are considered. It is shown that when the nutation of the angular momentum of an asymmetric top is stimulated in collisions with inert-gas atoms anomalies in the concentration dependences of the rotational-relaxation times can arise for certain states. The nonequilibrium rotational-level distribution in a supersonic water-vapor jet is described, and it is shown that the exchange RR processes occurring between the levels that form the edges of the rotational multiplets, under certain conditions, cause nonequilibrium distribution to appear. The relaxation characteristics of the Fermi-coupled $CO_2$ levels that arise as a result of the collisional stimulation of the corresponding intramolecular motion are considered.

## 1. INTRODUCTION

Of great interest at present is the study of molecular relaxation in low-density gas flows.[1–6] It is found that, under certain conditions, selective changes can be effected in the relaxation times of certain molecular states. These changes may be due to various causes, e.g., the formation of clusters under conditions of nonequilibrium condensation,[2] or the effect of "hot" molecules that penetrate the low-density gas jet.[7]

Reference 8 reports experimental results that indicate the selective variation of the relaxation time of the $2_{11}$ state of the rotational spectrum of the $D_2O$ molecule when atoms of the inert gas Ar are added. To explain their results, Bakastov *et al.*[8] assume that the selection rules, arising from the point-group symmetry of the molecule,[9] for collision-induced transitions in the rotational spectrum are not the same for atom-molecule and molecule-molecule collisions.

But it is shown in Ref. 10 that, in the case of molecules with the point group $C_{2v}$, these selection rules are the same for both molecule-atom and molecule-molecule collisions. The experimental data reported in Ref. 8 are explained by the assumption that the dominant transitions are the collision-stimulated transitions accompanied by a change in sign of the angular momentum component $K$ along the quantization axis fixed to the top. Additional selection rules are found for such transitions that, it turns out, are not the same for molecule-atom and molecule-molecule collisions.

In the present paper we show that the effectiveness of the $K \leftrightarrow -K$ collisional transitions is due to the stimulation of the intramolecular motion (nutation of the axis of rotation) in the asymmetric top. To describe the nutation, we use the method proposed by Braun[11] for solving trinomial recursion relations with slowly varying coefficients. Notice that, in the problem of the top, such relations arise when we go over to the representation whose basis vectors are the well-known Wigner $D$ functions. These relations are solved in Refs. 12 and 13 in the limit of large angular-momentum quantum numbers. But for a consistent explanation of the experimental results of Bakastov *et al.*[8] we should consider the nutation of the asymmetric top for arbitrary values of the angular momentum quantum number. The pertinent formulas are given in Sec. 2 below. In particular, we obtain expressions for the potential curves of the recursion relations and also describe how the characteristics of the nutation depend on the choice of the coordinate system $\mathscr{K}'$ rigidly fixed to the top.

The short-range forces that occur in a molecule-atom collision can, by deforming the potential curves, stimulate the nutation. The corresponding collisional selection rules are discussed in Sec. 3. In the case of the molecule-molecule collisions, because of the greater effective interaction range, stimulation of the asymmetric-top nutation does not occur.

It is well known[1] that the population of the rotational states in a planar supersonic rarefied water-vapor jet can have a nonequilibrium distribution, so that it cannot be described by a Boltzmann distribution with some rotational temperature. Let us note that the state of nonequilibrium obtains even in those cases when molecular-cluster-producing condensation does not occur in the jet. We show below that the cause of this state of nonequilibrium can be the exchange RR processes involving the levels that form the edges of the rotational multiplets. These levels in turn correspond to the approximately equidistant level sequences for systems with a tridiagonal Hamiltonian.[12] We find by analyzing the experimental data[1] the effective rotational temperatures characterizing the quasistationary population distribution over the states in a water-vapor jet.

In spite of the fact that the vibrational relaxation of the Fermi-coupled $10^00$ and $02^00$ states of the $CO_2$ molecule has been the subject of roughly a score of both experimental and theoretical investigations, there are at present no reliable data on the rate constants of the characteristic vibrational-exchange processes involving the lowest levels of the symmetric and deformed modes of the molecule.

Let us enumerate the principal characteristics of the vibrational relaxation of these states. The results reported in Refs. 14–24 indicate the existence of three characteristic temporal stages with constants $K_1 \gtrsim 10^6$ s$^{-1}$-Torr$^{-1}$, $K_2 \sim (2\text{–}4) \times 10^5$ s$^{-1}$-Torr$^{-1}$, and $K_3 \sim 2 \times 10^2\text{–}10^4$ s$^{-1}$-

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$\text{Torr}^{-1}$. The collisional processes corresponding to these stages have, however, not been explained. The situation is further complicated by the fact that the experiments reported in Refs. 18–24 can be described with the aid of just the characteristic excitation-level-dependent constant $K_3$.

The slowest of these three stages is governed by the *VT* processes involving states belonging to different vibrational multiplets of the $CO_2$ molecule. Note that the excitation-level dependence of the *VT*-relaxation rate has been investigated in the case of diatomic molecules ($O_2$)[25] and some polyatomic molecules ($CH_4$, $CD_4$, $SF_6$, $CH_3F$).[26–29] Note also that the absence of the relaxation processes characterized by the constants $K_1$ and $K_2$ in the experiments reported in Ref. 18–23 is due not only to the low response speed of the IR-radiation detector employed, but also to the small contribution to the phenomena in question (amplification or absorption in a nonequilibrium gas,[18–21] laser-radiation damping,[22] variation of the discharge glow in a gas as a result of IR-radiation absorption[23]) of fast processes of the type of the vibrational exchange with a small energy defect. The latter does not contradict the result of Stark's experiment,[24] in which the value $(1.4 \pm 0.5) \times 10^5\ \text{s}^{-1}\text{-Torr}^{-1}$ was obtained for the constant $K_2$ in a study of the small differences in the amplification relaxation for the transitions $10^00$–$00^01$ and $02^00$–$00^01$, which are due to the vibrational exchange involving the Fermi-coupled states.

More detailed information about the fast collision-governed processes of vibrational exchange with small energy defects can be extracted from Refs. 30–32, which report the measurement of the CARS spectrum of the $CO_2$ molecule under conditions of two-photon Raman excitation of the $10^00$ and $02^00$ levels. Note that the values found for the rate constants for the elementary processes differ sharply from the published theoretical values computed with allowance for the short-range[33,34] or long-range[35] forces in the interaction potential. Let us note in this connection that an attempt has been made before by Seeber[34] to relate the first two relaxation stages to stimulated Raman scattering (the absorption and emission of photons with wavelengths 10.6 and 9.6 μm) and the rotational relaxation of the sublevels of the $00^01$ vibrational level. But the first assumption contradicts the data reported in Refs. 15 and 17; the second, the data reported in the papers cited in Ref. 36, according to which the rotational relaxation of the above-noted sublevels is characterized by a constant $\sim 10^7\ \text{s}^{-1}\text{-Torr}^{-1}$.

We show in the present paper that the anomalies in the experimentally obtained[30–32] values for the rate constants of the vibrational exchange involving the $10^00$ and $02^00$ states can be attributed to the collisional stimulation of intramolecular motion of the Fermi resonance type. Then to the relaxation process with the constant $K_1$ correspond the processes of quasiresonace *VV* exchange involving $10^00$, $02^00$ and $11^10$, $03^10$ states, while to the relaxation process with the constant $K_2$ correspond the *VT*-relaxation processes involving the vibrational-multiplet sublevels not coupled by the Fermi interaction, which relaxation processes also have small energy defects. The rate constants of the latter processes are anomalously large because of the proposed collisional stimulation.

## 2. WAVE FUNCTION OF THE ASYMMETRIC TOP IN THE ANGULAR MOMENTUM REPRESENTATION

The rotational Hamiltonian of a molecule regarded as a solid can be obtained from the classical expression for the energy by replacing the squares of the rotational angular momentum components along the axes of the coordinate system $\mathscr{K}'$ rigidly fixed to the molecule by the corresponding operators. To find the explicit forms of the rotational angular momentum operators, it is convenient to use the Dirac method,[37] writing the expressions for the rotational angular momentum components along the axes of the system $\mathscr{K}'$ and the axes of the laboratory system $\mathscr{K}$ in terms of generalized coordinates—the Euler angles[38]—and generalized momenta. After deriving the expressions for the classical Poisson brackets, and using the well-known theorem proved by Dirac,[37] we find the commutation relations for the required operators. The commutation relations uniquely determine the operators for the rotational angular momentum components along the axes of the coordinate systems $\mathscr{K}'$ and $\mathscr{K}$. The explicit forms of these operators are obtained from the classical expressions for the rotational angular momentum components by replacing the generalized momenta by the usual differential operators.

Let $\langle \omega | JME \rangle$, where $\omega = \varphi, \theta$, and $\psi$ are the Euler angles, $J = 0, 1, 2, \ldots, M = -J, -J+1, \ldots, +J$ are the rotational angular momentum quantum numbers, and $E$ is the energy, be the wave function of the asymmetric top in the Euler-angle representation. Let us go over to the representation for which the basis vectors are the familiar Wigner $D$ functions.[38] We have

$$\langle \omega | JME \rangle = \sum_K \langle \omega | JMK \rangle \langle JMK | JME \rangle, \tag{2.1}$$

where $\langle \omega | JMK \rangle = D^J_{MK}(\omega)$ are the basis vectors and $\langle JMK | JME \rangle = a^{JE}_K$ is the wave function in the angular momentum representation. Using the explicit form of the Hamiltonian of the asymmetric top, we find for the coefficients $a^{JE}_K$ the equations

$$V^J_{K-1} a^{JE}_{K-2} + (G_K{}^J - E) a_K{}^{JE} + V^J_{K+1} a^{JE}_{K+2} = 0, \tag{2.2}$$

$$V^J_{K\pm1} = ((A-B)/4)\,[(J \pm K + 2)(J \pm K + 1)(J \mp K - 1)(J \mp K)]^{1/2},$$

$$G_K{}^J = ((A+B)/2)\,[J(J+1) - K^2] + CK^2,$$

where $A$, $B$, and $C$ are the rotational constants of the molecule. Let us introduce the notation $X^{JE}_K$ for the ratio $a^{JE}_K / a^{JE}_{K-2}$. Accordingly, from (2.2), we obtain

$$V^J_{K-1} + (G_K{}^J - E) X_K{}^{JE} + V^J_{K+1} X_K{}^{JE} X^{JE}_{K+2} = 0. \tag{2.3}$$

Let us, following Braun,[11–13] consider the solution to Eq. (2.3), assuming that $K$ runs through a continuous range of values. For $J \gg |K|$ the coefficients $V^J_{K\pm1}$ and $G^J_K$ in Eq. (2.3) are slowly varying functions of the variable $K$. Then in a certain range of values of the parameter $E$ we can neglect the difference between $X^{JE}_{K+2}$ and $X^{JE}_K$, and replace Eq. (2.3) by the simple quadratic equation

$$V^J_{K-1} + (G_K{}^J - E) X_K{}^{JE} + V^J_{K+1} (X_K{}^{JE})^2 = 0. \tag{2.4}$$

As shown in Ref. 11, this approximation is valid for values of the parameter $E$ sufficiently far removed from the turning points given by the equation $D(E) = 0$, where $D(E)$ is the discriminant of Eq. (2.4). Furthermore, the transition from Eq. (2.3) to Eq. (2.4) is possible in the regions far from the points $K = \pm J, \pm (J-1)$, which are the singular points for Eq. (2.2). Formally, we can obtain the solution in the vicinity of the singular points by making the substitutions[11]

$$V_{K+1}^{J} V_{K-1}^{J} \to (V_K{}^J)^2, \qquad (J \pm K)(J \pm K+1) \to (J+{}^1/_2 \pm K)^2. \tag{2.5}$$

For $D > 0$ one of the particular solutions to Eq. (2.2) will increase rapidly (exponentially), while the other will decrease rapidly, with varying $K$. The corresponding range of values of the parameter $E$ is called a classically forbidden region. The values $E_1 \equiv P_K^J = G_K^J + 2V_K^J$ and $E_2 \equiv Q_K^J = G_K^J - 2V_K^J$ obtained from the equation $D(E) = 0$ specify the boundaries of the classically allowed region of values of the parameter $E$. In this region the roots of Eq. (2.4) are complex conjugates of each other, with the corresponding moduli equal to unity. The solutions to Eq. (2.3) in the classically allowed region are oscillating functions of the variable $K$.

The expressions found by Braun for the potential curves $P_K^J$ and $Q_K^J$ with $J \gg 1$ can be written in the form

$$\begin{aligned} P_K{}^J &= A\left(J+\frac{1}{2}\right)^2 - (A-C)K^2, \\ Q_K{}^J &= B\left(J+\frac{1}{2}\right)^2 - (B-C)K^2. \end{aligned} \tag{2.6}$$

Let us consider the method of deriving the expressions for the potential curves that does not use the assumption that $J$ is large. We transform the familiar[39] recursion relations for the functions $d_{mn}^{l}(\pi/2)$, where $d_{mn}^{l}(\theta)$ is the Wigner function,[38] into the following form:

$$\begin{aligned} &\frac{1}{4}[(l+m-1)(l+m)(l-m+2)(l-m+1)]^{1/2} d_{m-2,n}^{l}\left(\frac{\pi}{2}\right) \\ &+\frac{1}{4}[(l-m-1)(l-m)(l+m+2)(l+m+1)]^{1/2} d_{m+2,n}^{l}\left(\frac{\pi}{2}\right) \\ &\qquad = \left\{n^2 - \frac{1}{2}[l(l+1)-m^2]\right\} d_{mn}{}^{l}\left(\frac{\pi}{2}\right). \end{aligned} \tag{2.7}$$

From (2.7) it follows that the function $i^K\, d_{KP}^{J}(\pi/2)$, where

$$P = \{A[J(J+1)-K^2] + CK^2 - E\}^{1/2}/(A-B)^{1/2}, \tag{2.8}$$

satisfies an equation whose coefficients coincide with the analogous coefficients of Eq. (2.2). Near a turning point the function $a_K^J$ is a slowly varying function of the variable $K$, and, consequently, we can set $d_{K\pm 2,\, P(K)}^{J} \approx a_{K\pm 2}^{J}$. After this, the expression for the potential curve is obtained with the use of the condition determining the turning point of the function $d_{mn}^{l}(\pi/2)$, and according to which[40]

$$mn = \pm\{[l(l+1)-m^2][l(l+1)-n^2]\}^{1/2}. \tag{2.9}$$

Substituting (2.8) into (2.9), we find

$$Q_K{}^J = BJ(J+1) - (B-C)K^2. \tag{2.10}$$

Notice that (2.10) goes over into (2.6) up to the well-known semiclassical approximation $(J+1/2)^2 \to J(J+1)$. Similarly, it can be shown that the function $\mathrm{d}_{KR}^{J}(\pi/2)$, where

$$R = \{E - B[J(J+1)-K^2] - CK^2\}^{1/2}/(A-B)^{1/2}, \tag{2.11}$$

satisfies an equation with coefficients equal to the coefficients in (2.2). Then for the potential curve we obtain the following expression:

$$P_K{}^J = AJ(J+1) - (A-C)K^2. \tag{2.12}$$

Near a turning point an arbitrary solution to Eq. (2.2) can be written in the form of a linear combination of the functions $i^K d_{KP}^{J}(\pi/2)$ and $d_{KR}^{J}(\pi/2)$, and, consequently, the expressions (2.10) and (2.12) are indeed the required potential curves.

Note that there is a case in which the above approximate method of finding the potential curves leads to the exact result. Let us compare the equation

$$pa_{\nu-1} + pa_{\nu+1} = 2a_\nu, \tag{2.13}$$

for which $p = p_* = 1$ at the turning point, with the equation for the Bessel function $J_\nu(p\nu)$:

$$pJ_{\nu-1}(p\nu) + pJ_{\nu+1}(p\nu) = 2J_\nu(p\nu). \tag{2.14}$$

Near the turning point we can set $a_{\nu\pm 1} \approx J_{\nu\pm 1}(p\nu)$ and, consequently, to find the value of $p_*$, we can use the condition determining the turning point for the Bessel function (see Appendix A). It is not difficult to verify that in this case the exact expression, equal to unity, is obtained for $p_*$.

Thus, the above analysis shows that Braun's semiclassical method is applicable in the case of rotational angular momentum quantum number values of order unity as well, in complete analogy with the well-known case of the harmonic oscillator.

Let us draw attention to the following circumstance. The solution found in Ref. 11 for the trinomial recursion relations in the vicinity of the turning point is not exact. This arises because, in the case of the recursion relations, in contrast to the differential equations, the expansion of the coefficients around some point that is not a singular point for the equation in question does not lead to a corresponding expansion of the solution. Only in the vicinity of the turning point, where the function is slowly varying, does the expansion of the coefficients yield an approximate representation of the solution. This assertion can easily be verified for an exactly soluble recursion relation.

In the particular case under consideration we can, by expanding the coefficients in Eq. (2.2) around the point $K = 0$, easily find the exact solution of the corresponding recursion relation in the form of the function $\mu^{a+\nu} F(a+\nu, b, c, z)$, where $\nu = 1/2K$ and $F(a, b; c; z)$ is the hypergeometric function; the parameters $\mu$, $a$, $b$, $c$, and $z$ are related in a definite manner with the expansion parameters for the coefficients in Eq. (2.2). After this, we can, by using the condition determining the turning points of the hypergeometric function (see Appendix A), obtain approximate numerical values for the potential curves $P_K^J$ and $Q_K^J$ for $K = 0$. Let us note that, for $J = 2$, the values obtained in this case differ from the analogous values found from the formulas (2.10) and (2.12) for the $D_2O$ molecule by 5.2 and 11.5%.

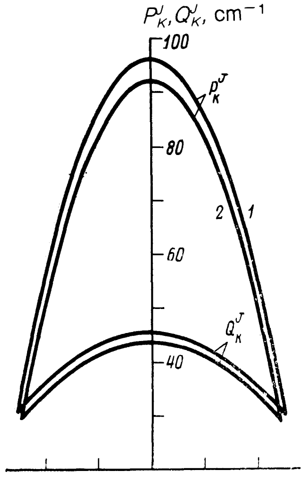

FIG. 1. Potential curves for the second multiplet of the $D_2O$ molecule (the $\mathscr{K}'$ system: $y' = C_2$, $z' \| OP$, and $OP \perp DOD$). 1) The semiclassical approximation; 2) exact computation.

The above form of the approximate solution of Eq. (2.2) can be used to compute those levels whose energies are close to the $P^J_K$ and $Q^J_K$ values at $K = 0$. For this purpose we use the well-known transformation formula for the hypergeometric function in the case when $Z > 1$:

$$F(a, b; c; z)$$

$$= \frac{\Gamma(c)\Gamma(b-a)}{\Gamma(b)\Gamma(c-a)}(-1)^a z^{-a} F\left(a, a+1-c; a+1-b; \frac{1}{z}\right)$$

$$+ \frac{\Gamma(c)\Gamma(a-b)}{\Gamma(c)\Gamma(c-b)}(-1)^b z^{-b} F\left(b, b+1-c; b+1-c; \frac{1}{z}\right). \quad (2.15)$$

Taking account of the fact that the phase of the wave function can always be chosen so that the coefficients $a^{JE}_K$ in (2.1) at energies corresponding to the asymmetric-top energy levels are real, we find with the aid of (2.15) the conditions determining the level energies:

$$\mu>0,\ b=0,\ -1,\ -2\ldots;\ \mu<0,\ c-b =0,\ -1,\ -2\ldots\ . \quad (2.16)$$

The formulas obtained correspond to the approximately equidistant sequences of energy levels for systems with a tridiagonal Hamiltonian.[12]

Let us consider certain consequences that follow from the form of the potential curves $P^J_K$ and $Q^J_K$. Let the system $\mathscr{K}'$ be chosen so that $A > B > C$. In the case of the $D_2O$ molecule this implies that the $y'$ axis coincides with the symmetry axis of the molecule, while the $z'$ axis is perpendicular to the plane of the molecule. Figure 1 shows the $P^J_K$ and $Q^J_K$ curves, as computed from the formulas (2.6), as well as (2.10) and (2.12), with $A = 15.383$ cm$^{-1}$, $B = 7.258$ cm$^{-1}$, $C = 4.849$ cm$^{-1}$ (Ref. 41), and the value $J = 2$. It can be seen that, at definite values of the parameter $E$, there are two classically alowed regions separated by a potential barrier. The wave functions for both the levels below the barriers and those above it are found to be symmetric or antisymmetric combinations of states differing in the sign of $K$. These superpositions arise because of the partial localization in $K$ space under conditions of subbarrier and above-the-barrier reflection from the potential barrier. Note that the classical or quantum nutation of the axis of rotation of the top corresponds to transmission above the barrier or beneath it.

An interesting feature of the problem under consideration is the doublet splitting of the above-barrier levels. It can be shown that, for $A > B > C$, the wave functions of the doublet levels have the same parity in $K$ space: in the $\omega$ representation they are superpositions of $D$ functions either with only even, or only odd, values of $K$, and the corresponding energies are equal when the above-barrier reflection is neglected.[13] Consequently, for the chosen orientation of the system $\mathscr{K}'$, the doublet splitting of the above-barrier levels is accounted for by the above-barrier reflection.

We should also point out the dependence of the form of the potential curves $P^J_K$ and $Q^L_K$ on the orientation of the system $\mathscr{K}'$ relative to the nuclear core of the molecule. In particular, following Braun, let us consider the quantization scheme in which $A < B < C$. For the $D_2O$ molecule this means that the $y'$ axis coincides with the axis of the molecule, while the $z'$ axis is parallel to the plane of the molecule. The potential curves for the present case are obtained from (2.10) and (2.12) by substituting the appropriate values for the rotational constants. It turns out in this case that those levels which previously were above the barrier levels are now subbarrier levels for the "inverted" barrier.[1)] Consequently, the doublet splitting noted above in the case of the $D_2O$ molecule can also be accounted for by tunneling in the direction parallel to the plane of the molecule.

Let us now consider the intermediate case when the $z'$ axis of the $\mathscr{K}'$ system is perpendicular to the $C_2$ symmery axis and makes an angle $\alpha$ with the plane of the molecule and the $y'$ axis is parallel to the $C_2$ axis. For such an orientation of the $\mathscr{K}'$ system the rotational Hamiltonian of the molecule has the following form:

$$\hat{H} = \tilde{A}\hat{J}_{x}{}^2 + B\hat{J}_{y'}{}^2 + \tilde{C}\hat{J}_{z'}{}^2 - D[\hat{J}_{x'}\hat{J}_{z'} + \hat{J}_{z'}\hat{J}_{x'}],$$

$$\tilde{A} = A\frac{1-(C/B)\chi^2}{1+\chi^2(A-C-AC/B)/B},$$

$$\tilde{C} = C\frac{1+(A/B)\chi^2}{1+\chi^2(A-C-AC/B)/B}, \quad (2.17)$$

$$D = \frac{AC\chi(1-\chi^2)^{1/2}}{B[1+\chi^2(A-C-AC/B)/B]},$$

where $\chi = \sin\alpha$. In the angular-momentum representation we obtain for the coefficients $a^{JE}_K$ the equation

$$V^J_{K-1}a^{JE}_{K-2} + F^{J+1/2}_{K-1/2}a^{JE}_{K-1} + (G_K{}^J - E)a_K{}^{JE}$$

$$+ F^{J+1/2}_{K+1/2}a^{JE}_{K+1} + V^J_{K+1}a^{JE}_{K+2} = 0, \quad (2.18)$$

$$V^J_{K\pm1} = {}^1/_4(\tilde{A}-B)[(J\pm K+2)(J\pm K+1)(J\mp K-1)(J\mp K)]^{1/2},$$

$$F^{J+1/2}_{K\pm1/2} = -{}^1/_2 D(2K\pm1)[(J\mp K)(J\pm K+1)]^{1/2},$$

$$G_K{}^J = {}^1/_2(\tilde{A}+B)[J(J+1)-K^2] + \tilde{C}K^2.$$

Going over to the variable $Z^{JE}_K = a^{JE}_{K-1}/a^{JE}_{K-2}$, we find

$$V_{K-1}^{J}+F_{K-1/2}^{J+1/2}Z_K^{JE}+(G_K^J-E)Z_K^{JE}Z_{K+1}^{JE}+F_{K+1/2}^{J+1/2}Z_K^{JE}Z_{K+1}^{JE}Z_{K+2}^{JE}$$
$$+V_{K+1}^{J}Z_K^{JE}Z_{K+1}^{JE}Z_{K+2}^{JE}Z_{K+3}^{JE}=0. \qquad (2.19)$$

For $J\gg 1$, neglecting the difference between $Z_{K\pm l}^{JE} <$ with $l\ll J$, and $Z_K^{JE}$, we obtain

$$V_{K-1}^{J}+F_{K-1/2}^{J+1/2}Z_K^{JE}+(G_K^J-E)(Z_K^{JE})^2$$
$$+F_{K+1/2}^{J+1/2}(Z_K^{JE})^3+V_{K+1}^{J}(Z_K^{JE})^4=0. \qquad (2.20)$$

In order to take account of the behavior of the function $Z_K^{JE}$ in the vicinity of the singular points, we transform the coefficients in Eq. (2.20) in the following manner:

$$V_{K\pm1}^{J}\to V_K^J,\quad F_{K\pm1}^{J+1/2}\to F_K^{J+1/2},$$
$$(J\pm K)(J\pm K+1)\to(J+{}^1/_2\pm K)^2. \qquad (2.21)$$

Accordingly, in place of Eq. (2.20), we find

$$\tilde{V}_K^J+\tilde{F}_K^JZ_K^{JE}+(\tilde{G}_K^J-E)(Z_K^{JE})^2+\tilde{F}_K^J(Z_K^{JE})^3$$
$$+\tilde{V}_K^J(Z_K^{JE})^4=0,$$
$$\tilde{V}_K^J={}^1/_4(\tilde{A}-B)[(J+{}^1/_2)^2-K^2],\qquad \tilde{F}_K^J=F_K^{J+1/2}, \qquad (2.22)$$
$$\tilde{G}_K^J={}^1/_2(\tilde{A}+B)[(J+{}^1/_2)^2-K^2]+\tilde{C}K^2.$$

It is well known that the nature of the roots of an algebraic equation of the fourth degree changes when the sign of the discriminant $D$ of its cubic resolvent is changed. In the case under consideration we find

$$D=-\frac{16}{108}[X+2+2|Z|][X+2-2|Z|][X-2-{}^1/_4Z^2],$$
$$X=\frac{\tilde{G}_K^J-E}{\tilde{V}_K^J},\qquad Z=\frac{\tilde{F}_K^J}{\tilde{V}_K^J}. \qquad (2.23)$$

The curves corresponding to the roots of the equation $D(E)=0$ have the following form:

$$P_K^J=\tilde{G}_K^J+2[\tilde{V}_K^J+|\tilde{F}_K^J|],\qquad H_K^J=\tilde{G}_K^J+2[\tilde{V}_K^J-|\tilde{F}_K^J|],$$
$$Q_K^J=\tilde{G}_K^J-2\tilde{V}_K^J-{}^1/_4(\tilde{F}_K^J)^2/\tilde{V}_K^J. \qquad (2.24)$$

In the energy plane they serve as boundaries of certain regions where the solutions to Eq. (2.22) exhibit essentially different behaviors. Figure 2 shows the $P_K^J$, $H_K^J$, and $Q_K^J$ curves for the $D_2O$ molecule in the case when $J=2$ and $\alpha=45°$. It is found that the classically allowed regions in the case under consideration are the regions designated as $A$ and $B$ in Fig. 2. In the region $A(D>0)$ Eq. (2.22) has two real and two complex conjugate roots with moduli equal to unity. In the region $B(D<0)$ Eq. (2.22) has two pairs of complex conjugate roots, the moduli of one of the two pairs being also equal to unity. In the classically forbidden region Eq. (2.22) does not possess complex roots with moduli equal to unity.

It can be seen from Fig. 2 that, for the given orientation of the $\mathscr{K}'$ system, there are two potential barriers—an ordinary barrier and an inverted one—separating the classically allowed regions. Notice that the vertices of the barriers coincide at a certain value of the angle $\alpha$, and, consequently, the doublet splitting for this orientation of the $\mathscr{K}'$ system will be entirely subbarrier transmission. Similarly, there exists an orientation of the $\mathscr{K}'$ system such that the double splitting is determined only by the characteristics of the above-barrier transmission. In particular, this obtains in the case when $A>C>B$. In the case of the $D_2O$ molecule this means that the $z'$ axis of the $\mathscr{K}'$ system coincides with the $C_2$ symmetry axis. It is easy to verify that, for $A>C>B$, the potential curves bound a convex figure having two quasibarriers. Accordingly, the doublet splitting arises as a result of the above-barrier reflection from the quasibarriers. Notice that the magnitude of the doublet splitting decreases with increasing distance from the vertices of the quasibarriers. The wave functions of the doublets in the $\omega$ representation are superpositions of $D$ functions with either only even or only odd values of $K$, each of the superpositions possessing a definite parity in $K$ space. The latter is due to the partial localization in $K$ space, this localization arising in the present case because in the vicinity of the quasibarrier vertices the intersecting curves have derivatives with opposite signs.

## 3. COLLISIONAL STIMULATION OF THE NUTATION OF THE ROTATION AXIS FOR ASYMMETRIC-TOP MOLECULES

It is well known[9] that the point-group symmetry of a molecule manifests itself in the existence of definite selection rules characterizing the nonspherical scattering. But besides the point-group symmetry for molecules having no optical antipodes, the invariance of the interaction under space inversion must be taken into account in the derivation of the selection rules. We shall show that the same type of limitations then arise for molecule-atom collisions as for molecule-molecule ones.

Let us determine the behavior under inversion of the matrices $D_{mk}^{l}(\omega)$ and the quantities $\beta_{lk}(\alpha_1\ldots\alpha_n)$ contained in the generalized multipole expansion of the nonspherical interaction.[9] Let us first of all note that the quantities $\beta_{lk}(\alpha_1\ldots\alpha_n)$, which characterize the shape of the nuclear configuration of the molecule may, in the general case, be pseudoscalar quantities. An exception is the case of a planar molecule, in which the inversion of the nuclei can be replaced by rotation through $\pi$ about an axis perpendicular

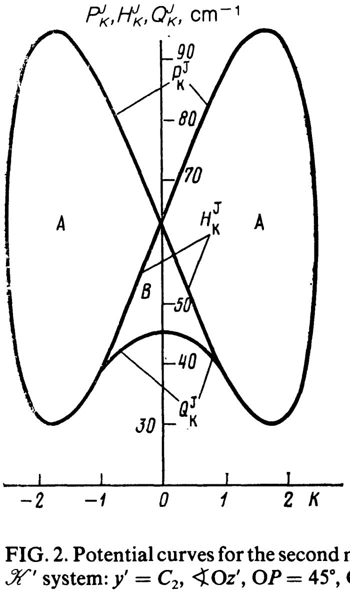

FIG. 2. Potential curves for the second multiplet of the $D_2O$ molecule (the $\mathscr{K}'$ system: $y'=C_2$, $\measuredangle Oz'$, $OP=45°$, $OP\perp DOD$).

to the plane of the molecule. Accordingly, if the molecule is rotated about the $z'$ axis, only those $\beta_{lk}$ for which $l+k$ is even will be nonzero.

For nonplanar, noncentrosymmetric molecules, the configuration that arises through inversion of the nuclear coordinates can be obtained from the original orientation through a combination of a rotation through an angle of $2\pi/n$ about a given $C_n$ axis (the number of rotoinversion axes and the values of $n$ depend on the point-group symmetry of the molecule) and a specific permutation of the equivalent nuclei. In the case when we can neglect the inversion splitting of the levels on account of the tunneling between the various nuclear configurations, we can also neglect the change that occurs in the interaction potential as a result of the transposition of the equivalent nuclei. In this case the quantities $\beta_{lk}$ should be taken to be scalar quantities, and the inversion operation should be taken to be equivalent to a rotoinversion.

After these remarks, we can determine through direct computation the nature of the limitations that arise when allowance is made for the invariance of the interaction under space inversion. For example, for the $NF_3$ molecule, which possesses the $C_{3v}$ point-group symmetry, we can show that, in the case when the $z'$ axis of the system $\mathscr{K}'$ fixed to the molecule is parallel to the $C_3$ axis and the $z'y'$ plane coincides with $\sigma_v$ symmetry plane, the corresponding condition is the equality $\beta_{lk} = \beta_{l,\,-k}$, and, what is more, that this condition applies both in the case of the molecule-atom interaction and in the case of the molecule-molecule interaction.

It is known from line-width measurements[41,43] that the molecule-molecule interaction has a significantly longer effective range than the molecule-atom interaction. Investigations carried out by the double-microwave-resonance method[44] have shown that in the first case the scattering is described largely by the dipole selection rules, while in the second case transitions are observed of "higher multipole order," and the parity selection rules are violated in the cases of such molecules as $NH_3$, HCN, and $CH_3OH$ (molecules with internal motion).

Let us assume that, for the case of asymmetric-top molecules being considered, the short-range forces that occur in the molecule-atom interaction can lead to the stimulation of the subbarrier of above-barrier $K \leftrightarrow -K$ transitions considered above. Let us find out the selection rules to which these transitions correspond. We represent the multipole expansion of the interaction terms responsible for the collisional stimulation of the nutation in the following form:

$$\mathscr{V}_\tau = \sum_l V_l \frac{1}{2}\left(t_l\hat{\tau} + \hat{\tau} t_l\right), \tag{3.1}$$

where $t_l$ is the partial term of the expansion of the nonspherical part of the molecule-atom interaction and the operator $\hat{\tau}$ is defined by the relation $\hat{\tau}|K\rangle = |-K\rangle$, the symmetrization being necessary because of the noncommutativity of $t_l$ and $\hat{\tau}$. It is easy to show that, in the $\omega$ representation, the asymmetric-top wave functions are the eigenfunctions of the operator $\hat{\tau}$, the corresponding eigenvalues being equal to $P$, where $P = \pm 1$. Using (3.1), we can find an additional selection rule for the collisions stimulating the nutation of the axis of rotation of the top[10]:

$$PP' = 1. \tag{3.2}$$

Notice that (3.2) forbids the collisional transitions $2_{20} \leftrightarrow 2_{11}$ and $2_{11} \leftrightarrow 2_{02}$. This enables us to explain the experimental result reported in Ref. 8. Let us emphasize that, although the values of the index $P$ for a level with a given energy depend on the choice of the system $\mathscr{K}'$, whether or not particular transitions will be forbidden in the nutation-stimulating collisions does not depend on the choice of the system $\mathscr{K}'$.

Finally, let us draw attention to the following circumstance. The operators $D^l_{mk}(\omega)$, which are contained in the nonspherical part of the molecule-atom interaction, and determine the nature of the collisional transitions in the rotational spectrum, form a complete set. In order to describe the $K \leftrightarrow -K$ collisional transitions, we must take into account the "remote" terms in the nonspherical interaction expansion, and carry out the summation in accordance with the perturbation-theory expansion for the scattering matrix. Instead of this, in Ref. 10 we suggest the use of an equivalent operator $\hat{\tau}$ having nonzero matrix elements between states differing in the sign of $K$. The rate of convergence of such a reduced nonspherical scattering-matrix expansion is similar to the rate of convergence of the nonspherical scattering-matrix expansion for linear molecules or molecules of the asymmetric top type, for which nutation of the axis of rotation does not occur. Thus, the introduction of the operator $\hat{\tau}$ corresponds to an effective regrouping of the nonspherical scattering-matrix expansion terms, which allows us to take account of the collisional stimulation of the intramolecular motion for molecules of the asymmetric-top type.

## 4. CHARACTERISTICS OF THE POPULATION DISTRIBUTION OVER THE STATES IN A WATER-VAPOR JET

It is possible that there exists another macroscopic effect that owes its origin to the energy-level structure of the asymmetric top, specifically, to the presence of roughly equidistant sequences of levels in the rotational spectrum. It is well known[13] that such sequences are formed by the levels located near the extremum points of the potential curve $P^J_K$ and $Q^J_K$ with $J \gg 1$, constituting the edges of the corresponding rotational multiplets. The exchange RR processes that occur between the levels under consideration can lead to a change in the relaxation rate of the individual molecular states, and this in turn manifests itself in the distortion of the Boltzmann distribution of the populations of the states. Let us note that the distortion of the shape of the Boltzmann distribution of the populations of the states has been observed in a rarefied water-vapor jet issuing from a supersonic nozzle into a vacuum.[1]

An experimental investigation of absorption under the conditions of a vapor jet yielded for the parameter characterizing the state of nonequilibrium the values

$$K = n_{12}/n_{12}(T). \tag{4.1}$$

Here $n_{12}$ is the difference between the populations of the pair of levels in question and $n_{12}(T)$ is the difference between the populations of the same levels under conditions when there

TABLE I.

| Temperature values, °K | Nonequilibrium parameter ratios | Calculation | Experiment |
|---|---|---|---|
| $T_{\rm tr} = 157.79$<br>$T_{\rm rot} = 175.58$<br>$T^{(1)}_{\rm rot} = 195.55$<br>$T^{(2)}_{rot} = 198.56$ | $\frac{K(2_{02}-2_{11})}{K(3_{31}-4_{22})}$ | 2,206 | 2,206 |
| | $\frac{K(2_{02}-2_{11})}{K(4_{31}-5_{24})}$ | 3,617 | 3,616 |
| | $\frac{K(3_{31}-4_{22})}{K(4_{31}-5_{24})}$ | 1,640 | 1,639 |

is equilibrium between the translational and rotational degrees of freedom:

$$n_{12}(T)=\frac{g_I}{Q(T)}[\exp(-\varepsilon_1/T)-\exp(-\varepsilon_2/T)], \qquad (4.2)$$

where $\varepsilon_1$ and $\varepsilon_2$ are the level energies, $Q(T)$ is the rotational partition function, and $g_I$ is the degree of degeneracy in terms of the nuclear spin. Let us, for the purpose of describing the data obtained by Bulatov *et al.*,[1] assume that the rotational temperature of the levels between which the resonance RR processes do not occur is equal to $T_{\rm rot}$, and that the corresponding temperature in the opposite case is equal to $\tilde{T}_{\rm rot}$. In particular, we shall assume that the rotational temperatures of the levels $1_{11}$, $2_{02}$, $2_{11}$, $4_{22}$, and $5_{24}$ are equal to $T_{\rm rot}$, while those of the levels $3_{31}$ and $4_{31}$ are equal to $-\tilde{T}^{(1)}_{\rm rot}$ and $\tilde{T}^{(2)}_{\rm rot}$. Notice that the difference between the temperatures $\tilde{T}^{(1)}_{\rm rot}$ and $\tilde{T}^{(2)}_{\rm rot}$ is due to the existence of a characteristic transition region. We present the computational data in Table I, in which we give the values of the translational temperature $T_{\rm tr}$ and the effective rotational temperatures $T_{\rm rot}$ and $\tilde{T}^{(1,2)}_{\rm rot}$ found from the values of the ratios of the nonequilibrium parameters for certain pairs of levels:

$$1_{11}-2_{02},\ 2_{02}-2_{11};\quad 1_{11}-2_{02},\ 3_{31}-4_{22};\quad 1_{11}-2_{02},\ 4_{31}-5_{24}. \quad (4.3)$$

Furthermore, in Table I we compare the experimental values for the ratios of the nonequilibrium parameters for the level pairs

$$2_{02}-2_{11},\ 3_{31}-4_{22};\quad 2_{02}-2_{11},\ 4_{31}-5_{24};\quad 3_{31}-4_{22},\ 4_{31}-5_{24} \quad (4.4)$$

with the corresponding values computed from the obtained rotational temperatures. The agreement, to within the limits of the experimental error, between the computed and experimental values attests the corrrectness of the assumptions made about the form of the parameters characterizing the state of nonequilibrium of the populations of the states in the water-vapor jet.

## 5. COLLISIONAL STIMULATION OF THE FERMI RESONANCE FOR THE MOLECULES OF CARBON DIOXIDE GAS

The rate constants found in CARS-spectrum analyses in Refs. 30–32 for the vibrational-exchange processes involving Fermi-coupled levels of the $CO_2$ molecule are given in Table II. It can be seen that, as compared to the characteristic rate of the *VV* exchange in the deformation mode, equal to $(2–4)\times10^5$ s$^{-1}$-Torr$^{-1}$ (reaction *C*), the rate of the *VT* process for the levels $10^00$ and $02^00$ is anomalously small [$\simeq 7\times10^4$ s$^{-1}$-Torr$^{-1}$ (reaction *A*)], while the rate of the analogous process for the levels $10^00$, $02^00$, and $02^20$, which are not coupled by a Fermi resonance, is, on the contrary, anomalously high, being roughly equal to $(4–7)\times10^5$ s$^{-1}$-Torr$^{-1}$. Let us emphasize accordingly that the high rate of the *VT* process involving the $10^00$ and $02^20$ levels in comparison with the rate of the *VT* process involving the $10^00$ and $02^00$ levels is, contrary to the assertion made in Refs. 30–32, not at all connected with the magnitude of the energy defect. Estimates also corroborate this assertion. In particular, those terms in the potential which contain the combination $Q^2_d = Q^2_{d,x} + Q^2_{d,y}$, where $Q_{d,x}$ and $Q_{d,y}$ are the normal coordinates of the deformation vibration, are responsible for the *VT* relaxation involving the levels $10^00$ and $02^00$. Similarly, we can describe the *VT* relaxation involving the $10^00$ and $02^20$ levels if we take into account in the potential the terms containing the combination $Q^2_d\cos^2\varphi$, where $\cos\varphi = Q_{d,x}/Q_d$. Using for the estimate the formula given in Ref. 45, and setting the coefficients of the indicated combinations equal, we find that, at $T = 300$ K and in the case when the constant in the exponential repulsive potential has the value 5 Å$^{-1}$, the rate of the *VT* process for the $10^00$ and $02^00$ levels is even greater than that of the *VT* process for the $10^00$ and $02^20$ levels.

We should also draw attention to the following circumstances.

TABLE II.

| | Vibrational exchange reactions in $CO_2$ | $K$ (in s$^{-1}$-Torr$^{-1}$) |
|---|---|---|
| *A* | $CO_2(10^0\,0)+CO_2(00^0\,0)\leftrightarrow CO_2(02^0\,0)+CO_2(00^0\,0)+103$ cm$^{-1}$ | $\leqslant 7\cdot10^4$ |
| *B* | $CO_2(10^0\,0)+CO_2(00^0\,0)\leftrightarrow CO_2(02^2\,0)+CO_2(00^0\,0)+53$ cm$^{-1}$<br>$CO_2(02^0\,0)+CO_2(00^0\,0)\leftrightarrow CO_2(02^0\,0)+CO_2(00^0\,0)-50$ cm$^{-1}$ | $(4–7)\,10^5$ |
| *C* | $CO_2(02^2\,0)+CO_2(00^0\,0)\leftrightarrow CO_2(01^1\,0)+CO_2(01^1\,0)+0{,}3$ cm$^{-1}$ | $(2–4)\,10^5$ |
| *D* | $CO_2(10^0\,0)+CO_2(10^0\,0)\leftrightarrow CO_2(20^0\,0)+CO_2(00^0\,0)-33$ cm$^{-1}$<br>$CO_2(02^0\,0)+CO_2(02^0\,0)\leftrightarrow CO_2(04^0\,0)+CO_2(00^0\,0)+22{,}5$ cm$^{-1}$ | Small |
| *E* | $CO_2(10^0\,0)+CO_2(01^1\,0)\leftrightarrow CO_2(11^1\,0)+CO_2(00^0\,0)-22$ cm$^{-1}$<br>$CO_2(02^0\,0)+CO_2(01^1\,0)\leftrightarrow CO_2(03^1\,0)+CO_2(00^0\,0)+19$ cm$^{-1}$ | $\gtrsim 7\cdot10^5$ |

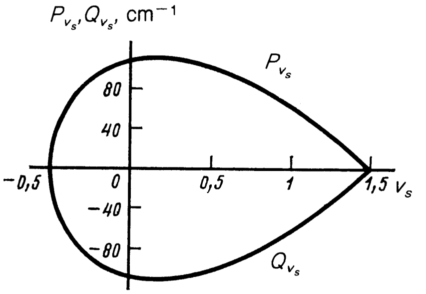

FIG. 3. Potential curves for the second multiplet of the $CO_2$ molecule.

1.The anomalously small value of the rate constant for the reaction $A$ agrees with the value of the rate constant for the analogous reaction

$$CO_2(10^01)+Ar \leftrightarrow CO_2(02^01)+Ar-12\ cm^{-1},^1$$

which Finzi and Moore[46] have found to have a rate $\lesssim 10^4$ $s^{-1}$-Torr$^{-1}$.

2. The value $(2–4)\times 10^5$ $s^{-1}$-Torr$^{-1}$ found for the reaction $C$ is close to the result obtained by Seeber[34] in numerical computations carried out using the well-known SSH theory.[47]

3. The rate-constant values for the reactions $E$ are close to the corresponding values for the analogous $VV$-exchange reactions

$$CO_2(10^00)+CO_2(00^01) \leftrightarrow CO_2(10^01)+CO_2(00^00)-22\ cm^{-1},$$

$$CO_2(02^00)+CO_2(00^01) \leftrightarrow CO_2(02^01)+CO_2(00^00)-21\ cm^{-1},$$

for which Finzi and Moore[46] have found the values $(4.2\pm 0.3)\times 10^6$ and $(3.9\pm 0.4)\times 10^6$ $s^{-1}$-Torr$^{-1}$. Note that in the last case the experimentally obtained rate-constant values are close to the theoretical values computed in Ref. 48 with allowance for the long-range attractive forces.

Let us, for the purpose of explaining the experimental data reported in Refs. 30–32, draw attention to the existence of intramolecular motion in the $CO_2$ molecule, when, because of the Fermi resonance, energy initially concentrated in a symmetric (deformation) vibration is transferred into a deformation (symmetric) vibration. We shall use Braun's method in the description. The nonzero matrix elements of the anharmonic combination $\tau_F = \text{const}\, xQ_sQ_d$ (where $Q_s$ is the normal coordinate of the symmetric vibration) responsible for the Fermi splitting have the following form

$$\langle v_s \pm 1; v_d \mp 2, l\,|\text{const}\, Q_sQ_d^2|v_s; v_d, l\rangle$$
$$= \tfrac{1}{2}w\{(v_s + \tfrac{1}{2} \pm \tfrac{1}{2})[(v_d + 1 \mp 1)^2 - l^2]\}^{1/2}, \tag{5.1}$$

where $w = 50.4\ cm^{-1}$ is the Fermi-resonance constant[49] and $\langle Q_s; Q_d, \varphi\,|v_s; v_d, l\rangle$ is the product of the corresponding harmonic functions. Using (5.1), we obtain for the coefficients $a_{v_s}$ contained in the expansion of the vibrational wave function of the molecule in terms of the harmonic functions the following equation:

$$N_{v_s}a_{v_s-1} + (G-E)a_{v_s} + N_{v_s+1}a_{v_s+1} = 0, \tag{5.2}$$

where

$$G = \tfrac{1}{2}\omega_s v + \omega_a v_a,$$
$$N_{v_s} = \tfrac{1}{2}\omega v_s{}^{1/2}[(v - 2v_s + 2)^2 - l^2],$$

$v = 2_{v_s} + v_d$ is the vibrational multiplet number, and $\omega_s = 2\omega_d$ and $\omega_a$ are the frequencies of the symmetric and antisymmetric vibrations. The potential curves $P_{v_s} = G + 2N_{v_s+1/2}$ and $Q_{v_s} = G - 2N_{v_{s+1/2}}$ for Eq. (5.2) bound a convex figure having two quasibarriers. In Fig. 3 we show as an example the potential curves for the second multiplet of the $CO_2$ molecule.[2)] Consequently, the appearance of the multiplet structure in the vibrational spectrum of the $CO_2$ molecule is due to reflection from the indicated quasibarriers. Notice that here, as in the above-considered case of the asymmetric top, a purely quantum effect occurs: above-barrier reflection from the quasibarriers.

Knowing the form of the potential curves, and using the formulas given in Ref. 12, we can obtain approximate analytic expressions for the energy levels forming the edges of the vibrational multiplet for given values of $v$ and $l$. For $l = 0$ we have

$$\varepsilon_N \approx \frac{1}{2}\omega_s + \omega_a v_a$$
$$\pm 2w\left(\frac{v+2}{6}\right)^{3/2}\left\{1-\left(N+\frac{1}{2}\right)\frac{3\sqrt{3}}{v+2}\right.$$
$$\left.+\left(N+\frac{1}{2}\right)^2\frac{15}{4(v+2)^2}\right\}, \tag{5.3}$$

where $N = 0, 1, 2, \ldots$ . Note that the formula (5.3) is accurate to within 11% in the case when $v = 2$, and to within 3% when $v = 4$.

Let us assume that the short-range forces responsible for the $VT$ relaxation can lead to the stimulation of the flow between the regions of partial localization located in the vicinities of the quasibarriers. To describe the collisional stimulation, we shall use an operator $\hat{\tau}$ whose matrix elements are nonzero only for the functions of one and the same multiplet, and coincide with the matrix elements of the anharmonic combination $\tau_F$. Notice that the vibrational wave functions of the molecule are the eigenfunctions of the operator $\hat{\tau}$, the corresponding eigenvalues being equal to $\Delta/\sqrt{2}$, where $\Delta$ is the level shift relative to the multiplet center. Let us represent the terms in the interaction potential that are responsible for the collisional stimulation as follows:

$$\mathscr{V}_\tau = \tfrac{1}{2}[\hat{\tau}t(Q_s; Q_d, \varphi; Q_a) + t(Q_s; Q_d, \varphi; Q_a)\hat{\tau}], \tag{5.4}$$

where $t$ is some function of the normal displacements of the atoms. For example, in the simplest case we can set $t(Q_s, Q_d, \varphi; Q_a) = \cos^2\varphi$. The form used for the interaction $\mathscr{V}_\tau$ leads to definite selection rules, according to which $\mathscr{V}_\tau$ does not make a contribution to the $VT$ transitions between the levels located at distances $\pm\Delta$ from the multiplet center (these levels are coupled by the Fermi interaction, e.g., the levels $10^00$ and $02^00$; $10^01$ and $02^01$, etc.). It is clear that the selection rules obtained allow us to explain the anomalies in the values of the rate constants of the $VT$ transitions between the vibrational-multiplet levels. Using the experimental data reported in Refs. 30–32, we estimated the order of the terms containing the combination $\hat{\tau}\cos^2\varphi$, and responsible for the collisional stimulation of the intramultiplet $VT$ relaxation. It was found that the indicated terms are roughly an order of magnitude greater than the terms containing the combination $Q_d^2$, and responsible for the $VT$ relaxation between the levels coupled by the Fermi intraction.

Notice that the collisional stimulation can lead to an increase not only in the $VT$-relaxation rates, but also in the $VV$-exchange rates. The form of the corresponding terms in the interaction is similar to (5.4):

$$\mathscr{V}_{\tau\tau_1}=\tfrac{1}{2}\{\hat{\tau}\hat{\tau}_1 t\,[Q_s;\,Q_d\varphi;\,Q_a;\,(Q_s;\,Q_d\varphi;\,Q_a)_1] + t\,[Q_s;\,Q_d\varphi;\,Q_a;\,(Q_s;\,Q_d\varphi;\,Q_a)_1]\hat{\tau}\hat{\tau}_1\}, \qquad (5.5)$$

where the subscript 1 pertains to the partner-particle in the collision. Indeed, the rate constant for the process $C$ with a small energy defect, that occurs between the $02^20$, $00^00$, and $01^10$ levels, whose energies are close to the corresponding values computed without allowance for the anharmonicity, differs little from the numerical value computed with allowance for the short-range repulsive forces.[34] At the same time the rate constants for the $E$ processes with much greater energy defects, in which the levels $10^00$, $11^10$, $02^00$, and $03^10$ "perturbed" by the Fermi interaction participate, have anomalously large values. It is possible that this increase is due to the short-range forces responsible for the collisional stimulation of the intramolecular motion, and not to the influence of the long-range attractive forces, which induce the vibrational-rotational transitions unaccompanied by distortion of the trajectory of the relative motion.[50]

vibrational-rotational transitions unaccompanied by distortion of the trajectory of the relative motion.[50]

Finally, let us note that the exchange reactions $D$ indicated in Table II can be described by taking account of the potential terms containing $Q_s$ or $Q_d^2$. According to experiment, the magnitudes of such terms are much smaller than those of the terms containing the combination $Q_d \cos\varphi$, and responsible for the $C$ and $E$ exchange reactions.

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## APPENDIX A

According to the well-known WKB method,[51] the point where the total and potential energies of a particle are equal is called a turning point. Using certain exact solutions to the one-dimensional Schrödinger equation, we find conditions on the indices of some special functions determining the boundaries of the characteristic classically allowed regions, where the solutions to the Schrödinger equation exhibit oscillating behavior. It is clear that these conditions determine the turning points of the special functions in question.

*1. The Bessel function*. The solutions to the Schrödinger equation in the one-dimensional field $U(x) = -U_0\exp(-|x|/a)$ can be expressed in terms of the Bessel functions. For $x > 0$ we have

$$\psi_E(x)=\mathrm{const}\,J_\nu\left[\left(\frac{8ma^2U_0}{\hbar^2}\right)^{1/2}\exp\left(-\frac{x}{2a}\right)\right], \qquad (A.1)$$

where $\nu = 2\varkappa a$, $E = -\hbar^2\varkappa^2/2\mathrm{m}$, $m$ is the particle mass, and $\hbar$ is the Planck constant. Using A.1, we obtain the condition determining the turning point of the Bessel function $J_\nu(z)$:

$$\nu=z. \qquad (A.2)$$

*2. The hypergeometric function*. It is in terms of the hypergeometric functions that we express the solutions to the Schrödinger equation in the one-dimensional field

$$U(x)=\frac{\hbar^2\alpha^2}{2m}\left[\frac{\varkappa(\varkappa-1)}{\sin^2\alpha x}+\frac{\lambda(\lambda-1)}{\cos^2\alpha x}\right], \qquad 0\leqslant x\leqslant\frac{\pi}{2\alpha}.$$

We have

$$\psi_E(x)=\mathrm{const}(\sin\alpha x)^{\varkappa}(\cos\alpha x)^{\lambda}F\left\{\frac{1}{2}\left(\varkappa+\lambda+\left(\frac{2mE}{\alpha^2\hbar^2}\right)^{1/2}\right),\ \frac{1}{2}\left(\varkappa+\lambda-\left(\frac{2mE}{\alpha^2\hbar^2}\right)^{1/2}\right);\quad \varkappa+\frac{1}{2};\ \sin^2\alpha x\right\}. \qquad (A.3)$$

In accordance with (A.3), the condition determining the turning points of the hypergeometric contribution function $F(a, b; c; z)$ will have the following form

$$\frac{(a+b-c)^2-1/4}{1-z}+\frac{(c-1)^2-1/4}{z}=(a-b)^2. \qquad (A.4)$$

*3. The confluent hypergeometric function*. The solutions to the Schrödinger equation in the one-dimensional field

$$U(x)=U_0\left(\frac{a}{x}-\frac{x}{a}\right)^2, \qquad x>0.$$

are expressed in terms of the confluent hypergeometric functions. We have

$$\psi_E(x)=\mathrm{const}\left\{\left(\frac{2mU_0}{\hbar^2a^2}\right)^{1/2}x^2\right\}^{s+1}\exp\left\{-\left(\frac{mU_0}{2\hbar^2a^2}\right)^{1/2}x^2\right\} \times\Phi\left\{s+\frac{1}{2}-\frac{ma(E+2U_0)}{2\hbar(2mU_0)^{1/2}};\ 2s+1;\ \left(\frac{2mU_0}{\hbar^2a^2}\right)^{1/2}x^2\right\}, \qquad (A.5)$$

$$s=\frac{1}{4}\left(\frac{8mU_0a^2}{\hbar^2}+1\right)^{1/2}.$$

We can, using (A.5), represent the condition determining the turning points of the confluent hypergeometric function $\Phi(a; b; z)$ in the following form:

$$\frac{2b-4a}{z}-\frac{(b-1)^2-1/4}{z^2}=1. \qquad (A.6)$$

Notice that, in deriving the conditions (A.2), (A.4), and (A.6), we took the particle energy $E$ to be a variable.

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[1)] Here and below we use the terminology introduced in Ref. 42.

[2)] It is assumed that the method used here to find the potential curves is effective also in the case when the values of the number $v$ are comparable to unity.

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[1] E. D. Bulatov *et al.*, Zh. Eksp. Teor. Fiz. **76**, 543 (1979) [Sov. Phys. JETP **49**, 274 (1979)].
[2] N. V. Karelov, A. K. Rebrov, and R. G. Sharafutdinov, Pis'ma Zh. Eksp. Teor. Fiz. **27**, 24 (1978) [JETP Lett. **27**, 21 (1978)]; Zh. Prikl. Mekh. Tekh. Fiz. No. 3, 3 (1978).
[3] N. V. Borzenko, N. V. Karelov, A. K. Rebrov, and R G. Sharafutdinov, Zh. Prikl. Mekh. Tekh. Fiz. No. 5, 20 (1976).

[4] K. Bergmann, U. Hefter, and P. Herring, Chem. Phys. **32**, 1 (1978).

[5] G. Luiks, S. Stolte, and J. Reuss, Chem. Phys. **62**, 217 (1981).

[6] M. Faubel and E. R. Weinar, J. Chem. Phys. **75**, 641 (1981).

[7] R. Q. Sharafutdinov, in: Rarefied Gas Dynamics: Proc. Seventh Intern. Symposium, Pisa, Italy, 1971, Vol. 1.

[8] S. S. Bakastov, V. K. Konyukhov, and V. I. Tikhonov, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 427 (1983) [JETP Lett. **37**, 506 (1983)].

[9] V. D. Borman, A. S. Bruev, L. A. Maksimov, and B. I. Nikolaev, Teor. Mat. Fiz. **13**, 241 (1972); Zh. Eksp. Teor. Fiz. **72**, 2100 (1977) [Sov. Phys. JETP **45**, 1103 (1977)].

[10] A. S. Bruev, Zh. Eksp. Teor. Fiz. **86**, 2056 (1984) [Sov. Phys. JETP **59**, 1195 (1984)].

[11] P. A. Braun, Teor. Mat. Fiz. **37**, 355 (1978).

[12] P. A. Braun, in: Voprosy kvantovoĭ teorii atomov i molekul (Problems of the Quantum Theory of Atoms & Molecules), Vol. 2, Leningrad State University, 1981, p. 240.

[13] P. A. Braun and A. A. Kiselev, Vvedenie v teoriya molekulyarnykh spektrov (Introduction to the Theory of Molecular Spectra), Leningrad State University, 1983, p. 105.

[14] C. K. Rhodes, M. J. Helly, and A. Javan, J. Chem. Phys. **48**, 5730 (1968).

[15] T. A. de Temple, D. R. Suhre, and P. D. Coleman, Appl. Phys. Lett. **22**, 349 (1973).

[16] R. R. Jacobs, K. J. Pettipiece, and S. J. Thomas, Phys. Rev. A **11**, 54 (1975).

[17] R. K. Huddleston and E. Weitz, Chem. Phys. Lett. **83**, 174 (1981).

[18] R. J. Carbone and W. J. Witteman, IEEE J. Quantum Electron. **QE-5**, 442 (1969).

[19] W. A. Rosser, E. Hoag, and E. T. Gerry, J. Chem. Phys. **57**, 4153 (1972).

[20] E. R. Murray, C. H. Kruger, and M. Mitchner, J. Chem. Phys. **62**, 388 (1975).

[21] D. J. Eckstrom and D. Bershader, J. Chem. Phys. **53**, 2978 (1970).

[22] K. Bulthuis, J. Chem. Phys. **58**, 5786 (1973).

[23] M. C. Gover and A. I. Carswell, Appl. Phys. Lett. **22**, 321 (1973).

[24] E. E. Stark, Appl. Phys. Lett. **23**, 335 (1973).

[25] S. A. Losev, O. P. Shatalov, and M. S. Yalovik, Dokl. Akad. Nauk SSSR **195**, 585 (1970) [Sov. Phys. Dokl. **15**, 1037 (1971)].

[26] S. A. Akhmanov, V. M. Gordienko, A. V. Mikheenko, and V. Ya. Panchenko, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 603 (1977) [JETP Lett. **26**, 453 (1977)].

[27] S. A. Akhmanov *et al.*, Izv. Akad. Nauk SSSR Ser. Fiz. **43**, 379 (1979); Zh. Eksp. Teor. Fiz. **78**, 2171 (1980) [Sov. Phys. JETP **51**, 1087 (1980)].

[28] K. S. Rutkovskiĭ and K. G. Tokhadze, Zh. Eksp. Teor. Fiz. **75**, 408 (1978) [Sov. Phys. JETP **48**, 204 (1978)].

[29] E. N. Chesnokov, V. N. Shcherbinina, and V. N. Panfilov, Zh. Eksp. Teor. Fiz. **75**, 2066 (1978) [Sov. Phys. JETP **48**, 1039 (1978)].

[30] A. M. Brodnikovsky, S. M. Gladkov, and N. I. Koroteev, Opt. Commun. **40**, 312 (1982).

[31] S. M. Gladkov, M. G. Karimov, and N. I. Koroteev, Pis'ma Zh. Eksp. Teor. Fiz. **35**, 381 (1982) [JETP Lett. **35**, 470 (1982)].

[32] A. M. Brodnikovskiĭ, S. M. Gladkov, M. G. Karimov, and N. I. Koroteev, Zh. Eksp. Teor. Fiz. **84**, 1664 (1983) [Sov. Phys. JETP **57**, 971 (1983)].

[33] K. F. Herzfeld, J. Chem. Phys. **47**, 743 (1967).

[34] K. N. Seeber, J. Chem. Phys. **55**, 5077 (1971).

[35] R. D. Sharma, J. Chem. Phys. **49**, 5195 (1968).

[36] P. K. Cheo and R. L. Abrams, Phys. Lett. **14**, 47 (1969); **15**, 177 (1969).

[37] P. A. M. Dirac, *The Principles of Quantum Mechanics*, Clarendon Press, Oxford, 1947 (Russ. Transl., Nauka, Moscow, 1979, p. 117).

[38] A. Bohr and B. R. Mottelson, *Nuclear Structure*, Benjamin-Cummings, New York, 1969 (Russ. Transl., Mir, Moscow, 1971, p. 75).

[39] I. M. Gel'fand, R. A. Minlos, and Z. Ya. Shapiro, Predstavleniya gruppy vrashcheniĭ i gruppy Lorentsa (Rotation- and Lorentz-Group Representations), GIFML, 1958, p. 103.

[40] V. V. Tolmachev, Kvaziklassicheskoe priblizhenie v kvantovoĭ mekhanike (The Semiclassical Approximation in Quantum Mechanics), Izd. MGU, 1980, p. 53.

[41] C. H. Townes and A.L. Schawlow, *Microwave Spectroscopy*, McGraw-Hill, New York, 1955 (Russ. Transl., IIL, Moscow, 1959, pp. 634 & 327.

[42] P. A. Braun and E. A. Solov'ev, Zh. Eksp. Teor. Fiz. **86**, 68 (1984) [Sov. Phys. JETP **59**, 38 (1984)].

[43] G. Birnbaum, Adv. Chem. Phys. **12**, 488 (1967).

[44] T. Oka, Adv. At. Mol. Phys. **9**, 127 (1973).

[45] A. S. Bruev and V. K. Konyukhov, Khim. Fiz. **3**, 46 (1984).

[46] J. Finzi and C. B. Moore, J. Chem. Phys. **63**, 2285 (1975).

[47] R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, J. Chem. Phys. **20**, 1591 (1952).

[48] J. C. Stephenson and C. B. Moore, J. Chem Phys. **56**, 1295 (1972).

[49] M. V. Vol'kenshteĭn, M. A. El'yashevich, and B. I. Stepanov, Kolebaniya molekul (Molecular Vibrations), Vol 1, GITTL, 1949, p. 598.

[50] R. D. Sharma and C. A. Brau, J. Chem. Phys. **50**, 924 (1969).

[51] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics,), Nauka, Moscow, 1974 (Eng. Transl., Pergamon, Oxford, 1977), p. 198.

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