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Properties of rotational transitions during collisions between molecules

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Possible rotational relaxation channels in a molecular gas that can be described by selection rules for nonspherical scattering are considered. It is shown that the selection rules for nonspherical scattering can be either exact or approximate. In the former case, the rules are due to some general symmetry properties of the interaction between the molecules; in the latter case, they are due to the dynamics of the particles and, in particular, they depend on the ratio of the moments of inertia of the molecules and on departures from equilibrium in the gas. It is shown that the selection rules obtained in this paper do not differ significantly from the Born-scattering selection rules. Selection rules are obtained for rotational transitions that are forbidden in the case of scattering by an atom, but are possible for scattering by a molecule.

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1. INTRODUCTION

Rotational relaxation in a polyatomic gas, i. e., the redistribution of rotational-level populations as the system tends to the equilibrium state may occur as a result of the complicated character of the nonspherical interaction between the molecules along different channels. The existence of several rotational relaxation channels in polar gases (for example, CH_3CN, CH_3F, C_2H_5CN) is indicated by experiments on the anomalous Senftleben effect.[1,2] Gordiets *et al.* have discussed the possibility of a laser for the microwave band, using the rotational transitions of molecules for which the probabilities of excitation transfer with $\Delta J \neq 0$ and $\Delta K \neq 0$ on collision are different (J and K are the angular momentum and the angular momentum component along an internal axis).

The number of possible relaxation channels, and the relationship between the probabilities of excitation transfer, are determined by the selection rules for transitions between rotational levels during collisions between molecules. These selection rules can be governed by general symmetry principles, for example, time reversal, inversion, and point symmetry of the molecule. Moreover, as will be shown below there may be selection rules governed by the dynamics and interaction of the molecules.

The description of rotational relaxation in the polyatomic case encounters definite difficulties because of the absence of adequate experimental data on the nonspherical scattering of molecules[4,5] and because of the complexity of highly nonequilibrium kinetic problems. Several papers have been published in recent years on the inelastic scattering of polar molecules, investigated by double microwave-microwave[5] and infrared-microwave resonance.[6–9] These methods consist of measuring the change in the absorption of microwave radiation corresponding to a definite transition between rotational levels whose population changes as a result of the application of the pump radiation at the transition frequency between two other levels (rotational or vibrational-rotational), and collisional transitions between pairs of levels. By retuning the frequency of the incident microwave radiation and measuring the absorption in the presence of the pump radiation, it is possible to determine the set of rotational states occupied by the excited molecules after collisions. As a result of such studies, and studies by the method of modulated double microwave resonance,[10,11] it has been possible to establish collisional selection rules for a number of polar molecules.

The selection rules are discussed by Oka[5] in the Born approximation. This discussion makes use of the nonspherical model scattering potential[12] which takes into account all the possible types of electrostatic interaction, and the selection rules follow from symmetry considerations which yield the nonzero multipole moments in the potential. The resulting selection rules describe inelastic transitions accompanying collisions between certain polar molecules. It is well known that collisions between polyatomic molecules, for which $\Delta E\tau_c/\hbar \ll 1$[3] ($\tau_c$ is the collision time and ΔE is the energy of the rotational transitions) can be strong. The description of such collisions must take into account the terms in the expansion of the $\mathcal{T}$ matrix after the first Born term. In this paper, we shall obtain an expression for the $\mathcal{T}$ matrix for an arbitrary Born approximation. The interaction between the molecules will be described by the model potential put forward by Hess *et al.*[13] for diatomic molecules and in our previous paper[14] for molecules with arbitrary point symmetry.

By nonspherical interaction, we understand the dependence of the potential on the orientation of the molecules regarded as rigid bodies. In contrast to the paper by Oka,[5] we shall determine the nonspherical part of the potential exclusively from symmetry considerations. We shall show that collisions between polyatomic molecules should be subject to selection rules determined by their point symmetry. The selection rules obtained in this way will show that rotational relaxation in a polyatomic gas can proceed along several channels, where the number of channels and the inelastic character of the corresponding collisions depend both on the ratio of the moments of inertia of the molecules and on the macroscopic conditions under which the relaxation process takes place.

2. WAVE FUNCTIONS FOR MOLECULES WITH ROTATIONAL DEGREES OF FREEDOM

Consider a monatomic molecule with rotational degrees of freedom. For simplicity, we shall confine our attention to molecules in the form of a symmetric spherical top. In the adiabatic approximation for the operator $\hat{H}$ describing the internal degrees of freedom, we have

$$\hat{H}=\hat{H}_{\mathrm{rot}}+\hat{H}_{\mathrm{int}}, \quad \hat{H}_{\mathrm{rot}}=B\hat{J}^2+(C-B)\hat{J}_{z'}^2, \tag{2.1}$$

where B, C are the rotational constants of the molecule, $\hat{J}_i$, (i', x', y', z') are the operators corresponding to the projections of the angular momentum along axes attached to the molecule, and $\hat{H}_{\mathrm{int}}$ describes the internal motion of the nuclei in the molecule.

We shall regard the molecule as a rigid body and will let $\hat{\mathbf{L}}=0$, where $\hat{\mathbf{L}}$ is the internal angular momentum operator. We note that, in the case of nonplanar molecules, this approximation is valid only for those molecules for which there is an inversion doubling of rotational levels, i.e., there is a sufficiently high barrier between the two potential minima corresponding to the two equilibrium positions of the nuclei obtained from one another by inverting all the nuclei at the center of gravity.[15] For plane and linear molecules, this inversion is replaced by the rotation of the molecule as a whole, and there is no inversion doubling. The definition of inversion for the Euler angles $\{\alpha, \beta, \gamma\}$ defining the orientation of the molecules is not unambiguous. We shall follow the definition adopted in molecular spectroscopy,[16] according to which inversion corresponds to

$$\{\alpha, \beta, \gamma\} \to \{\pi+\alpha, \pi-\beta, \pi-\gamma\}, \tag{2.2}$$

which, in turn, corresponds to the rotation of the coordinate system (x', y', z') attached to the molecule through an angle π about the y' axis. Under the above assumptions, the eigenfunctions of the operator $\hat{H}$ that have definite internal parity P can be written as follows:

$$\begin{gathered}\langle\omega|JKPM\rangle=\frac{i^J[J]}{4\pi}2^{-1/2}\{D_{MK}^J(\omega)+\eta D_{M-K}^J(\omega)\},\\ [J]=(2J+1)^{1/2},\quad \eta=(-1)^{[J+K+f(J,K)]+\xi},\quad P=\xi+f(J,K),\end{gathered} \tag{2.3}$$

where $D_{MK}^J(\omega)\equiv D_{MK}^J(\alpha, \beta, \gamma)$ is the finite rotation matrix,[16] $\xi=0.1$ ($\xi=0$ for $K=0$), and the factor $f(J,K)$ is introduced in order to obtain the correct parity for the rotational levels: for a prolate symmetric top $f(J,K)=J+K$ and for oblate symmetric top $f=K$.[15] For a flat symmetric top, $f=K$, $\xi=0$.

3. NONSPHERICAL INTERACTION OF MOLECULES WITH ROTATIONAL DEGREES OF FREEDOM

A. Interaction with a spherical particle

We shall assume that the nonspherical potential $\mathcal{V}$ depends on the vectors $\mathbf{a}_i$, $i=1, \ldots, n$, characterizing the positions of the n atoms in the molecule relative to the center of mass, and the position vector $\mathbf{r}$ joining the centers of mass to the colliding particles. In view of this, we shall write

$$\mathcal{V}=\sum_l V_l(r)\,[B_l(\mathbf{a}_i)\cdot Y_l(\mathbf{r})], \tag{3.1}$$

where $Y_{lm}(\mathbf{r})$ is a spherical harmonic of rank l, which depends on the orientation of the vector $\mathbf{r}$, and $B_{lm}(\mathbf{a}_i)$ is a spherical tensor also of rank l, constructed from the vectors $\mathbf{a}_i$ and invariant under the symmetry transformations of the molecules. We have

$$B_{lm}(\mathbf{a}_i)=\sum_p \beta_{lp}(\alpha_i)D_{mp}^l(\omega), \tag{3.2}$$

where $\beta_{lp}(\alpha_i)$ is the value of $B_{lm}(\mathbf{a}_i)$ in the coordinate system attached to the molecule.

The quantities $\beta_{lp}(\alpha_i)$ characterize the shape of the given molecule and are independent of orientation. They must be chosen so that the functions in (3.2) do not change under the corresponding transformations Γ of the point symmetry group of the molecules. The explicit form of such invariant combinations

$$\sum_p \beta_{lp}D_{mp}^l \tag{3.2$'$}$$

is given elsewhere.[14] Since the potential is real, we can use the properties of the function $D_{mp}^l(\omega)$ to show that

$$\beta_{lp}^*(\alpha_i)=(-1)^p\beta_{l-p}(\alpha_i). \tag{3.3}$$

The expressions given by (3.2) and (3.3) enable us to rewrite the potential $\mathcal{V}$ that is invariant under the inversion of the coordinates I in the form

$$\mathscr{V}={}^1/_2(\mathscr{V}+\mathscr{V}^I)=\sum_l V_l(r)\,\mathrm{Re}\,t_l,$$

$$\mathrm{Re}\,t_l=\sum_{m,p}\mathrm{Re}\,\beta_{lp}(\alpha_i)D_{mp}{}^l(\omega)Y_{lm}{}^*(\mathbf{r}). \qquad (3.4)$$

B. Interaction with the molecule

The above invariant combination (3. 2′) will now be used to write the interaction potential for two nonspherical molecules in the following form:

$$\mathscr{V}={}^1/_2(\mathscr{V}+\mathscr{V}^I)=\sum_{ll_1L}V_{ll_1L}(r)\,[\mathrm{Re}\,t_{ll_1L}-\mathrm{Im}\,t_{ll_1L}],$$

$$\mathrm{Re}\,t_{ll_1L}=\sum_{\substack{pp_1mm_1\\M}}\mathrm{Re}\,\beta_{lp}D_{mp}{}^l\,\mathrm{Re}\,\beta_{l_1p_1}D^{l_1}_{m_1p_1}\langle lm\,l_1m_1|LM\rangle Y_{LM}{}^*(\mathbf{r}), \qquad (3.5)$$

$$\mathrm{Im}\,t_{ll_1L}=\sum_{\substack{pp_1mm_1\\M}}\mathrm{Im}\,\beta_{lp}D\quad{}^l\,\mathrm{Im}\,\beta_{l_1p_1}D^{l_1}_{m_1p_1}\langle lml_1m_1|LM\rangle Y_{LM}{}^*(\mathbf{r})$$

where the subscript 1 refers to the partner molecule in the collisions.

The function $V_{ll_1L}(r)$ in (3. 5) has the following properties:

$V_{ll_1L}(r)=0$ if $l+l_1+L$ is odd, and

$V_{ll_1L}(r)=(-1)^L V_{ll_1L}(r)$ if the molecules are identical.

Comparison of (3. 4) with (3. 5) will show that the interaction described by the second term in (3. 5) is forbidden by symmetry considerations in the case of scattering by a spherical particle.

C. Matrix elements of the potential

In the case of interaction with a spherical particle, the matrix elements of the potential are

$$\langle\mathbf{k}'n'|\mathscr{V}|\mathbf{k}n\rangle=\iint d\mathbf{r}\,d\omega\langle\mathbf{k}'n'|\mathbf{r}\omega\rangle\mathscr{V}\langle\mathbf{r}\omega|\mathbf{k}n\rangle,$$
$$\langle\mathbf{r}\omega|\mathbf{k}n\rangle=\langle\mathbf{r}|\mathbf{k}\rangle\langle\omega|n\rangle. \qquad (3.6)$$

The functions $\langle\omega|n\rangle$ are given by (2. 3) and

$$\langle\mathbf{r}|\mathbf{k}\rangle=\sum_s A_s(kr)\sum_t Y_{st}{}^*(\mathbf{k})Y_{st}(\mathbf{r}),\qquad A_s(kr)=i^s(2/\pi)^{1/2}j_s(kr), \quad (3.7)$$

where $i_s(x)$ is the spherical Bessel function.

Using (2. 3), (3. 4), (3. 6), and (3. 7), we obtain

$$\langle\mathbf{k}'n'|\mathscr{V}|\mathbf{k}n\rangle=\sum_{S'Sl}A_{S'Sl}(k'k)\frac{[J']}{[J]}(-i)^{\Delta J}f_{S'Sl}\,\mathrm{Re}\,g_l,$$

$$A_{S'Sl}(k'k)=\pi^{-1/2}\frac{[S']}{[S]}[l](-i)^{\Delta S}\langle S'0l0|S0\rangle\int_0^\infty r^2\,dr\,j_{S'}(k'r)j_S(kr)V_l(r),$$

$$f_{S'Sl}=\sum_{t't}\langle J'M'J-M|l\Delta M\rangle\langle S't'S-t|l\Delta M\rangle Y_{S't'}(\mathbf{k}')Y_{S-t}(\mathbf{k}), \qquad (3.8)$$

$$\mathrm{Re}\,g_l=[1+(-1)^{l+\Delta P}]\{\langle J'K'J-K|l\Delta K\rangle\,\mathrm{Re}\,\beta_{l\Delta K}+\eta\langle J'K'JK|l\Sigma K\rangle\,\mathrm{Re}\,\beta_{l\Sigma K}\}.$$

The above expression for $f_{S'Sl}$ represents the dependence of the matrix element of the potential on the angle variables in the laboratory coordinate system, and the expression for $\mathrm{Re}g_l$ gives the dependence on the internal angle variables defined in the coordinate system attached to the molecule.

Similarly, for the molecule-molecule interaction, we have

$$\langle\mathbf{k}'n_{12}'|\mathscr{V}|\mathbf{k}n_{12}\rangle=\sum_{S'Sll_1L}A_{S'Sll_1L}(k'k)\frac{[J'][J_1']}{[J][J_1]}(-i)^{\Delta J+\Delta J_1}$$
$$\times f_{S'Sll_1L}(\mathrm{Re}\,g_l\,\mathrm{Re}\,g_{l_1}-\mathrm{Im}\,g_l\,\mathrm{Im}\,g_{l_1}),$$

$$A_{S'Sll_1L}(k'k)=\pi^{-1/2}\frac{[S']}{[S]}[L](-i)^{\Delta S}\langle S'0L0|S0\rangle\int_0^\infty r^2\,dr\,j_{S'}(k'r)j_S(kr)V_{ll_1l}(r),$$

$$f_{S'Sll_1L}=\sum_{t't\mu}\langle J'M'J-M|l\Delta M\rangle\langle J_1'M_1'J_1-M_1|l_1\Delta M_1\rangle$$
$$\times\langle l\Delta Ml_1\Delta M_1|L\mu\rangle\langle S't'S-t|L\mu\rangle Y_{S't'}(\mathbf{k}')Y_{S-t}(\mathbf{k}), \qquad (3.9)$$

$$\mathrm{Im}\,g_l=[1-(-1)^{l+\Delta P}]\{\langle J'K'J-K|l\Delta K\rangle\mathrm{Im}\,\beta_{l\Delta K}+\eta\langle J'K'JK|l\Sigma K\rangle\mathrm{Im}\,\beta_{l\Sigma K}\}.$$

We note that, in contrast to (3. 8), the expression given by (3. 9) includes $\mathrm{Im}g_l$. The dependence on the nonspherical variables to which this expression corresponds is forbidden by symmetry considerations in the case of interaction with a spherical particle. We also note that the formulas given by (3. 8) and (3. 9) can also be used for the scattering matrix within the framework of the well-known Born approximation.

4. SELECTION RULES FOR NONSPHERICAL SCATTERING

To investigate the properties of the scattering matrix, we shall use the well-known Born series

$$\mathscr{T}=\mathscr{V}+\mathscr{V}G^{(0)}\mathscr{V}+\mathscr{V}G^{(0)}\mathscr{V}G^{(0)}\mathscr{V}+\ldots, \qquad (4.1)$$

where $G^{(0)}=(E-H+i\delta)^{-1}$ is the Green function for a free particle. The expressions for the nonspherical part of the scattering matrix can be obtained with the aid of (3. 8) and (3. 9), using the general transformation rules for spherical tensors. However, for a molecule in the form of a symmetric top, one must take into account the fact that the rotational energy of the molecule depends on the square of the projections of the angular momentum along the axis of the top and, consequently, the matrix elements of the $G^{(0)}$ will, in general, contribute to the nonspherical part of the $\mathscr{T}$ matrix. In this case, the operator $\hat{H}_{\mathrm{rot}}$ has the form

$$\hat{H}_{\mathrm{rot}}=\hat{H}_{\mathrm{rot}}{}^S+\hat{H}',\quad \hat{H}_{\mathrm{rot}}{}^S=B\hat{J}^2,\quad \hat{H}'=(C-B)J_{z'}{}^2. \qquad (4.2)$$

Let $G_S^{(0)}$ represent the Green function corresponding to the operator $\hat{H}_{\mathrm{rot}}^S$. In this case, we have the following formal equation:

$$G^{(0)}=G_S^{(0)}+G_S^{(0)}\hat{H}'G^{(0)},$$

the iteration solution of which is

$$G^{(0)}=G_S^{(0)}+G_S^{(0)}\hat{H}'G_S^{(0)}+G_S^{(0)}\hat{H}'G_S^{(0)}\hat{H}'G_S^{(0)}+\ldots \qquad (4.3)$$

Substituting (4. 3) in (4. 1), we obtain $\mathscr{T}=\mathscr{T}^{(0)}+\mathscr{T}^{(1)}+\ldots$,

$$\mathscr{T}^{(0)}=\mathscr{V}+\mathscr{V}G_S^{(0)}\mathscr{V}+\mathscr{V}G_S^{(0)}\mathscr{V}G_S^{(0)}\mathscr{V}+\ldots, \qquad (4.4)$$
$$\mathscr{T}^{(1)}=\mathscr{V}G_S^{(0)}\hat{H}'G_S^{(0)}\mathscr{V}+\mathscr{V}G_S^{(0)}\hat{H}'\mathscr{V}G_S^{(0)}\mathscr{V}+\mathscr{V}G_S^{(0)}\mathscr{V}G_S^{(0)}\hat{H}'G_S^{(0)}\mathscr{V}+\ldots$$

The operators $\mathscr{T}^{(1)}$, $\mathscr{T}^{(2)}$, ... are useful only for prolate tops for which $C/B>1$. In view of this, let us begin by considering the nonspherical part of the matrix elements of the operator $\mathscr{T}^{(0)}$. Using (3. 8), (3. 9), and (4. 4), and transforming the expressions for the moments, we find that the nonspherical part of the matrix elements of this operator is determined by the expression $f_{s's\chi}\,\mathrm{Re}\,g_F$ for scattering by a spherical particle, and $f_{s'sXX_1Y}[\mathrm{Re}\,g_F\,\mathrm{Re}\,g_{F_1} - \mathrm{Im}\,g_F\,\mathrm{Im}\,g_{F_1}]$ for scattering by a molecule. Moreover, the values of XX_1YF may be substantially different from the corresponding values of ll_1Ll in (3.8) and (3.9) when a large number of terms in the expansion for the operator $\mathcal{T}^{(0)}$ is taken into account. The selection rules for nonspherical scattering are determined by the structure of the expression for $\mathrm{Re}\,g_F$ in the case of scattering by a spherical particle. In the case of scattering by a molecule, there may be additional selection rules described by the expression for $\mathrm{Im}\,g_F$. The selection rules due to the point symmetry of the molecules are determined by the properties of the quantities $\beta^F_{\Delta K}(\alpha_i)$. As an example, let us consider the scattering of a planar molecule having the symmetry D_{3h} by a spherical particle. For molecules with this symmetry (for example, BF_3), the nonspherical expansion contains only those β^F_p for which[14]

$$F=0,\ 2,\ 3,\ 4,\ldots;\ \ P=3\varkappa,\ \ \varkappa=0,\ \pm1,\ \pm2,\ldots;\ \ [F+P]-\ \text{even},$$
$$\beta_{3\varkappa}{}^F=(-1)^F\beta^F_{-3\varkappa}. \tag{4.5}$$

The following selection rules are obtained with the aid of (3.8) and (4.5):

$$\begin{gathered}\Delta K=3\varkappa,\quad |\Delta K|\leqslant F,\quad |\Delta J|\leqslant F,\\ [F+\Delta K]-\ \text{even};\quad [F+\Delta P]-\ \text{even}.\end{gathered} \tag{4.6}$$

In deriving the selection rules given by (4.6), we consider transitions for which $\mathrm{sign}\,K=\mathrm{const}$, i.e., there is no change in the direction of the molecular axis of rotation on collision. Such transitions are described by the first terms in (4.5). The remaining terms describe collisions in which the direction of the rotational axis of the molecule does change. The selection rules in this case are analogous to (4.6) with ΔK replaced by ΣK. Table I gives the selection rules for molecules with different symmetry.

In the case of molecule-molecule scattering, there may be certain additional allowed transitions, the selection rules for which are determined by the properties of the quantities $\mathrm{Im}\,g_F$. It is interesting to note that, for the above molecules with the symmetry D_{3h}, additional selection rules are forbidden by the properties of point symmetry. However, such transitions are allowed for molecules of lower symmetry (for example, C_{nv}). Table II identifies these transitions for molecules of different symmetry.

TABLE I.

Symmetry group	Selection rule
C_{nv}, $n=3.5$	$\Delta K=2n\varkappa$, $[\Delta P+\Delta F]$ — even
C_{nv}, $n=4.6$	$\Delta K=n\varkappa$, $[\Delta P+F]$ — even
C_{nh}, D_{nh}, $n=3.5$	$\Delta K=n\varkappa$, $[\Delta P+\Delta K]$ — even
C_{nh}, D_{nh}, $n=4.6$	$\Delta K=n\varkappa$, ΔP — even
D_{nd}, $n=3,4,5,6$	$\Delta K=2n\varkappa$, ΔP — even
T_d, O_h	$\Delta K=4\varkappa$, ΔP — even
$C_{\infty v}$	$[\Delta J+F]$, $[\Delta P+F]$ — even
$D_{\infty h}$	ΔJ, ΔP — even

TABLE II.

Symmetry group	Selection rule
C_{nv}, $n=3.5$	$\Delta K=n(2\varkappa+1)$, $[\Delta P+F]$ — odd
C_{nh}, $n=3.5$	$\Delta K=n\varkappa$, $[\Delta P+\Delta K]$ — odd
C_{nh}, $n=4.6$	$\Delta K=n\varkappa$, ΔP — odd
D_{nd}, $n=3.5$	$\Delta K=n(2\varkappa+1)$, ΔP — odd
D_{nd}, $n=4.6$	$\Delta K=n(2\varkappa+1)$, ΔP — odd
T_d	$\Delta K=2(2\varkappa+1)$, ΔP — odd

Note: (Table I and Table II): $\varkappa=0,\pm1,\pm2,\ldots$. For all molecules $|\Delta J|\leqslant\min(F,x)$, $|\Delta K|\leqslant F$.

We can show with the aid of (4.4) that the structure of the expressions determining the selection rules does not change when the operators $\mathcal{T}^{(1)}$, $\mathcal{T}^{(2)}$ are taken into account and, consequently, the above selection rules are general.

The selection rules obtained above for nonspherical scattering are due to the general symmetry properties of the scattering matrix and are, therefore, universal in character. Moreover, when effects in a molecular gas are investigated, the contributions of different types of collision are determined by statistically averaged collision probabilities. There are then additional restrictions on the possible types of collision due to the specific form of the distribution function for the molecules in the gas. It is clear that the character of these restrictions depends on whether the phenomena under consideration occur under equilibrium or nonequilibrium conditions.

Rotational levels with $J\gg1$ are excited for most molecular gases at room temperature. Using the asymptotic expression for the Clebsch-Gordan coefficients,[17] we can rewrite $\mathrm{Re}\,g_F$ and $\mathrm{Im}\,g_F$ as follows:

$$\begin{gathered}\mathrm{Re}\,g_F\approx[1+(-1)^{F+\Delta P}](-1)^{J-K}\frac{[F]}{[J]}\{\mathrm{Re}\,\beta_{\Delta K}{}^F d^F_{\Delta K,\Delta J}(x)+\eta\,\mathrm{Re}\,\beta_{\Sigma K}{}^F d^F_{\Sigma K,\Delta J}(x)\},\\ \mathrm{Im}\,g_F\approx[1-(-1)^{F+\Delta P}](-1)^{J-K}\frac{[F]}{[J]}\{\mathrm{Im}\,\beta_{\Delta K}{}^F d^F_{\Delta K,\Delta J}(x)+\eta\,\mathrm{Im}\,\beta_{\Sigma K}{}^F d^F_{\Sigma K,\Delta J}(x)\},\end{gathered} \tag{4.7}$$

where $x=K/J$, and $d^l_{mn}(x)$ is the Wigner function. It is clear that the contributions of different rotational transitions with $\Delta J\neq0$ and $\Delta K\neq0$ are determined by averaging the quantities $\mathrm{Re}\,g_F$ and $\mathrm{Im}\,g_F$ with the appropriate distribution functions. In thermal equilibrium, averaging over x yields:

$$\begin{gathered}\langle\mathrm{Re}\,g_F\rangle_0=\sum_{x=-1}^{+1}\mathrm{Re}\,g_F(x)\exp\left[-\frac{J^2}{T}(C-B)x^2\right],\\ \langle\mathrm{Im}\,g_F\rangle_0=\sum_{x=-1}^{+1}\mathrm{Im}\,g_F(x)\exp\left[-\frac{J^2}{T}(C-B)x^2\right].\end{gathered} \tag{4.8}$$

For an oblate symmetric top ($C\ll B$), the leading terms in (4.8) are those with $x\sim\pm1$, while for a prolate symmetric top $x\ll1$ ($C\gg B$). In the former case, the most important contribution to the effect is that due to collisions of molecules in states with $K\sim\pm J$. If we use the fact that

$$d_{mn}{}^l(1)=\delta_{mn}\ \text{and}\ d_{mn}{}^l(-1)=\delta_{m-n},$$

we find that, in the case under consideration, the allowed collisions are those for which

$$\Delta J=\pm\Delta K. \tag{4.9}$$

For a molecule in the form of a symmetric top, the minimum nonzero value is $\Delta K=3$ (for molecules with symmetry C_{3v}). Such collisions are described by the nonspherical term in the expansion of the scattering matrix with $F \geqslant 3$. In the case of slightly nonspherical objects, it is reasonable to suppose that such terms are much smaller than the first terms with $F=1, 2$. Consequently, in this approximation, for molecules in the form of an oblate symmetric top, we may conclude that the contribution of inelastic collisions is small. Rotational relaxation occurs slowly (in the case of small deviations from equilibrium) and is characterized by a single channel with $|\Delta J|=|\Delta K|=3$.

When $x \ll 1$, the most important are collisions between molecules in states with $|K| \ll J$. In this case, the properties of the functions $d^l_{mn}(0)$ [17] demand that

$$\begin{aligned}&[F+\Delta J] - \text{even for } : \Delta K=0,\\ &[F+\Delta K] - \text{even for } : \Delta J=0.\end{aligned} \tag{4.10}$$

It is clear from (4.10) that, in contrast to the case of molecules in the form of an oblate symmetric top, the terms in the nonspherical expansion of the scattering matrix with $F=1$ describe only inelastic collisions with $\Delta J=\pm 1$ for the molecules under consideration. It follows that, for molecules in the form of a prolate symmetric top, and for small deviations from equilibrium, rotational relaxation takes place rapidly and is characterized by several channels. In particular, we note the fastest channel ($\Delta J=\pm 1$, $\Delta K=0$) and the slowest channel ($\Delta J=\pm 1$, $\Delta K=\pm 3$). The corresponding terms in the nonspherical expansion of the scattering matrix that are responsible for relaxation have $F=1$ and $F=3$.

Averaging over x for $J \gg 1$ can be given a more graphic form if we recall that the effective values x_{eff} in (4.8) for $F \ll J$ are not very dependent on the behavior of the functions $\operatorname{Re} g_F(x)$ and $\operatorname{Im} g_F(x)$, which are power functions of x. In view of this, we substitute

$$x_{\text{eff}}=\pm\langle x^2\rangle^{1/2}. \tag{4.11}$$

For thermal equilibrium, we obtain

$$\langle x^2\rangle_0=[2C/B+1]^{-1} \tag{4.12}$$

and, consequently, when $C \gg B$, we have $x_{\text{eff}} \ll 1$. When $C \sim B$, we have $x_{\text{eff}} \sim 1/3$, and when $C \ll B$, $x_{\text{eff}} \sim \pm 1$. This is in agreement with the above formulas. In the absence of thermal equilibrium, for example, in the presence of pump radiation, $\langle x^2\rangle$ differs from (4.12) and depends on the character of the departure from equilibrium. The relative contribution of different channels to the relaxation process under nonequilibrium conditions is a function of the pump intensity and character. For example, for molecules in the form of an oblate symmetric top and a strong pump, we have the possibility of additional fast relaxation channels. We also note that, for dipole molecules in an electric field, the nonequilibrium addition to the equilibrium distribution function depends on x if there is a temperature or velocity gradient.[18] By varying the field strength or the macroscopic gradient, it is then possible to modify the energy transfer between translational and rotational degrees of freedom. This is of undoubted interest when a gas of dipolar molecules is used as the active medium in a source of coherent radiation.

Several authors have reported experimental studies of rotational transitions occurring during molecular collisions.[5–11] For example, for collisions of CH_3Cl molecules, Frenkel *et al.*[8] have observed the following rotational transitions:

$$\begin{aligned}&(a)\ \Delta J=1,\ \Delta K=0;\ \sigma^a \gg \sigma^b,\\ &(b)\ \Delta J \geqslant 1,\ \Delta K=3.\end{aligned} \tag{4.13}$$

The CH_3Cl molecules have the symmetry C_{3v}. If we compare (4.13) with the selection rules for molecules with symmetry C_{3v} (Table I), we note that transitions (a) can be described by retaining the term with $F=1$, whereas transitions (b) can be described by retaining the term with $F=3$. The small cross sections for transitions (b) as compared with (a) suggest that the nonspherical expansion for the scattering matrix converges rapidly. More detailed analysis of the experimental results is outside the scope of the present paper because, as noted above, this analysis must take into account the fact as to whether the rotational transitions are observed under equilibrium or nonequilibrium conditions.

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Measurements of the ion energy spectrum in a collisionless neutral current sheet

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A multichannel electrostatic energy analyzer has been used with a θ-pinch installation with a reverse field to determine the ion energy distribution in the radial and longitudinal directions in the plasma. A well-defined beam of ions reflected elastically from the sheet propagates in the radial direction ahead of the neutral sheet. The ion temperature in the sheet does not exceed 60–80 eV. The ion flux along the neutral sheet consists of ions scattered out of the radial flux and ions accelerated across the boundary between the hot and cold plasma.

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Determination of the energy spectra of particles in current sheets with lines of zero magnetic field is a topical problem in connection with attempts to explain some of the phenomena observed in cosmic plasma. They include processes in solar flares and in the tail of the earth's magnetosphere in which, as indicated by existing observational data, neutral current sheets play an important role in particle heating and acceleration. On the other hand, this problem is also connected with the question of turbulent heating of hot plasmas to thermonuclear temperatures at which binary collisions cannot ensure rapid energy dissipation.

It is desirable to elucidate the properties of particle spectra that are characteristic for neutral current sheets, and the physical processes responsible for these properties. Simulation experiments may be helpful in choosing theoretical models of the above phenomena.

Laboratory simulation of processes occurring in neutral current sheets have been described, for example, by Kawashima and Ohyabu,[1] Frank,[2] and Altyntsev and Krasov.[3] The relatively simplest of these experiments is that using the θ-pinch in the configuration of a piston field H_1 and an opposite quasistationary field H_0 frozen into the plasma. In this configuration,[4] measurements of the energy distribution in the electron component of the plasma show that the neutral current sheet is a source of electrons accelerated to energies of about 15 keV. The same configuration has been used to examine the dynamics of the ion components by measuring the Doppler broadening and emission line shift,[5] which indicate the presence of nonthermal particles whose origin is associated with the elastic reflection of a fraction of the ions from the magnetic piston.

In this paper, we report measurements of the energy distribution of the ion component of plasma using the fast charge-transfer atoms leaving the neutral current sheet in longitudinal and transverse directions.

APPARATUS AND DIAGNOSTICS

The experiments were carried out on the θ-pinch installation UN-Phoenix,[6] a diagram of which is shown in Fig. 1. Hydrogen plasma with concentration $n_0 = 2\times10^{12}-2\times10^{13}$ cm^{-3} and frozen-in quasistationary field $-H_0 = 150-600$ Oe was produced in the cylindrical glass chamber 1 (diameter 16 cm, length 100 cm). The plasma was compressed by the growing magnetic piston whose field H_1 was opposite in direction to H_0 ($H_1 \uparrow\downarrow H_0$) and was produced by discharging a low-inductance capacitor through the shock coil 4 (length 30 cm) surrounding the central part of the vacuum chamber. The amplitude of the magnetic field of the piston was typically 1200 Oe and the rise time was $T/4 = 400$ nsec. For $|H_1| > |H_0|$ after the piston was switched on, a cylindrical current sheet with a zero field line separating the regions of oppositely directed magnetic fields was produced in the plasma and traveled in the radial direction toward the chamber axis. Depending on the initial density n_0 of the plasma and the quasistationary field H_0, a rarefaction or compression wave propagated ahead of the neutral sheet.

The main parameters of the current sheet in the plasma (width Δ, velocity U, amplitude of magnetic field discontinuity ΔH) were measured with two magnetic probes with an open loop, 3 mm in diameter. The probes were placed successively along the radius of the system at distances $r_1 = 30$ mm and $r_2 = 42$ mm from the axis. The operational control of the initial plasma density n_0 during the measurement process was achieved with the aid of a microwave interferometer ($\lambda = 4$ mm).

The initial electron temperature T_e^0, estimated from microwave absorption in plasma,[7] was 0.5–1.0 eV. The ion temperature T_i^0 was not measured directly, but it was expected that $T_i^0 = T_e^0$ since the lifetime of the plasma (approximately 50 μsec) prior to the introduction of the piston was greater than the temperature relaxation time.