Rotational-State Dependence of the Collisional Pumping Rate for Astrophysical Masers

Isao SHIMAMURA

The Institute of Space and Astronautical Science
Komaba, Tokyo 153

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We study rotational-vibrational pumping and rotational-vibronic pumping by nonreactive collisions. The maser molecules are assumed to be linear, symmetric-top or asymmetric-top rotators. We apply the energy-sudden approximation with respect to the rotational motion. The rates for pumping to various different rotational states are expressible in a simple form; it includes the rotational energy and a small number of overall collision rate constants rather than the set of the individual rotational-vibrational (rotational-vibronic) rate constants. For pumping to low-lying rotational states \( r' \) the rates prove to be independent of \( r' \). This agrees with a result obtained by Watson et al. for the special case of rotational-vibrational pumping of a linear rotator. We discuss validity of the energy-sudden approximation and modifications that are necessary for purely rotational pumping of a dipolar molecule by a charged particle.

§ 1. Introduction with summary

1.1. Introduction to the subject

Since the first detection of the OH maser in Orion seventeen years ago, observations have revealed hundreds of interstellar and circumstellar maser sources.¹ These astrophysical masers provide a useful diagnostic of the phenomena in regions of unusual excitation conditions, if the pumping mechanisms for the masers are known in detail.² In any study of the pumping mechanisms the rate for pumping by nonreactive collisions should be compared with the rates for pumping by other mechanisms. Many authors have done this and have pointed out the importance of the collisional pumping. Especially, SiO masers associated with late-type stars appear to be pumped by nonreactive collisions.³

The rate for collisional pumping to a rotational-vibrational (or a fine-structure) level depends on the cross sections for many rotational-vibrational (or fine-structure) transitions in atom-molecule or molecule-molecule collisions. Each of these state-specified cross sections is difficult to measure or to calculate to a reasonable accuracy. Therefore, reliable estimation of the collisional pumping rate is usually prevented by the difficulty in obtaining the entire set of relevant cross sections with an accuracy and at energies necessary for this purpose.

Watson et al.,⁴ in their study of SiO masers, have discussed a theorem useful for the estimation of the rate. They have considered collisional pumping of
diatomic molecules in general in a $^1\Sigma$ state and in a hot gas. Then knowledge of the *individual* rotational-vibrational cross sections is unnecessary for calculating the rate for pumping to a low rotational level; only an *overall* cross section, which is independent of the rotational level, enters into the expression for the pumping rate associated with a specified vibrational transition. Thus, the collisional pumping rate is independent of the final rotational state, if it is a low-lying state. This result simplifies an understanding of the pumping mechanisms, because the number of parameters determining the pumping rate decreases greatly, and because the necessary overall cross sections are much easier to calculate or to measure than the set of individual cross sections. Furthermore, according to the rotational-state independence of the collisional pumping rate, population inversion occurs, if the decay of a rotational state due to any mechanism other than nonreactive collisions is faster for a lower state than for an upper state.

The purpose of the present paper is to extend the discussion by Watson et al. into more detail and to show more general results; see § 1.4 for summary.

1.2. The rate for pumping by nonreactive collisions

Assume that the molecules emitting maser radiation (referred to as maser molecules) have well-defined and uncoupled vibrational ($v$) and rotational ($\Gamma$) states. Let $\Gamma$ specify a set of degenerate rotational states. A diatomic or a linear polyatomic molecule in a $^1\Sigma$ state may be represented by a linear rotor, and its rotational state may be specified by $J$ and $M$ ($-J \leq M \leq J$), the quantum numbers for the rotational angular momentum and its projection onto a space-fixed axis of quantization. The rotational energy $E_\Gamma$ is $BJ(J + 1)$, $B$ being the rotational constant having the dimension of energy; the $2J + 1$ rotational states ($J$, $M$) having a $J$ in common are all degenerate. Thus $\Gamma$ denotes $J$ in this case. (For other cases see § 2.3.) Throughout this paper, $E_\Gamma$ is measured from the ground rotational state ($\Gamma = 0$).

Consider a rotational-vibrational transition of the molecule from state $(v, \Gamma)$ to state $(v', \Gamma')$ in collisions with an atom at collision energy $E$. The corresponding velocity is denoted by $V$. The rate constant for this collisional transition is an average of the product of $V$ and the cross section $\sigma(v' \Gamma'\leftarrow v\Gamma; E)$ over the Maxwellian distribution of $V$ at gas temperature $T_g$:

$$K(v' \Gamma'\leftarrow v\Gamma; T_g) = \langle V \cdot \sigma(v' \Gamma'\leftarrow v\Gamma; E) \rangle.$$  \hspace{1cm} (1)

Average over the initial degenerate states and summation over the final degenerate states are implicit here.

Initially the molecules occupy many different rotational states. The collision rate constant is to be averaged over the rotational distribution. Assume that the molecules are in rotational equilibrium at temperature $T_r$. Although the rotational temperature $T_r$ is often equal to the gas temperature $T_g$, we shall
distinguish between them to know clearly which temperature is relevant to which part of the collisional pumping rate. The number density $n_{v\Gamma}$ of the molecules in state $(v, \Gamma)$ shows the Boltzmann distribution

$$n_{v\Gamma}(T_r) = N_v g_{v\Gamma} \exp(-E_{v\Gamma}/kT_r), \quad (2)$$

proportional to the statistical weight $g_{v\Gamma}$ of the state $\Gamma$ and including a normalization constant $N_v$ and the Boltzmann constant $k$. Important to the maser action is the population of the level $(v', \Gamma')$ per degenerate sublevel. Thus we discuss the collisional pumping rate $P(v'\Gamma' \rightarrow v; T_h, T_r)$ per unit volume per unit time for excitation from vibrational state $v$ to a sublevel of $(v', \Gamma')$. We have

$$P(v'\Gamma' \rightarrow v; T_h, T_r) = N_p (g_{v'}^{-1} \sum_{\Gamma} n_{v\Gamma}(T_r) K(v'\Gamma' \rightarrow v\Gamma'; T_h) \quad (3)$$

with $N_p$ the number density of the particles that collide with the maser molecules. Often most molecules are in their ground vibrational state $(v=0)$. Then, only excitation from $v=0$ is important. The arguments in this paper, however, hold for a general $v$.

1.3. Rotational-invariance rule by Watson et al.

Watson et al.’s discussion starts from Eq. (3) for the collisions of linear rotators with atoms. They note that only small values of $\Gamma'$ (=$J'$) are relevant to the known SiO masers, and assume that, for small $J'$, small values of $\Gamma'$ (=$J$) must dominate the sum over $\Gamma$. Then, for high rotational temperature, $\exp(-E_{v\Gamma}/kT_r)$ in Eq. (2) is nearly unity, which makes the sum in Eq. (3) a simple, degeneracy-weighted sum of the collision rate constants. Watson et al. also note that, for high enough $T_h$, most collisions are sudden compared with the rotational motion of the molecules. Then, one may use a scaling-relations formula that expresses $\sigma(v'J' \rightarrow vJ)$ as a linear combination of $\sigma(v'J' \rightarrow v0)$ for $|J-J'| \leq J \leq (J+J')$, the coefficients for the linear combination involving the Clebsch-Gordan coefficients. (See, for example, Refs. 5-8.) Assuming that the energy of the relative motion in the final channel is independent of the rotational channel, and using formulas for the Clebsch-Gordan coefficients, Watson et al. explicitly compute the sum over $\Gamma$ with a result independent of $J'$. They also derive the $J'$-independence rule for collisions between two linear rotators.

1.4. Summary

1. The present paper stresses that Watson et al.’s derivation of the $J'$-independence rule is equivalent to a combination of two well-known consequences of the rotational-sudden approximation, namely, a rotational sum rule and the principle of detailed balance for the rotational degrees of freedom (§§ 2.1 and 2.2).

2. Then, an immediate generalization of the rotational-independence rule is
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possible for spherical-top, symmetric-top and asymmetric-top rotators (§ 2.4).

3. Without restriction to low rotational states $I'$, i.e., without the assumption that $\exp(-E_r/kT_r) \approx 1$, the collisional pumping rate takes a simple form. It depends on $I'$, and does not include the individual rotational-vibrational cross sections $\sigma(v'I'\leftarrow vI'; E)$, but includes overall cross sections that are common to all rotational states (§ 2.5).

4. A kinematic factor dependent on the rotational channel appears in the expression for the cross section in terms of the scattering amplitude. Correction for this factor, disregarded by Watson et al., is made to the lowest order (§ 2.6); the discussion in the Appendix serves for this purpose.

These results are quite general.

5. They apply not only to the pumping rate itself but also to the individual contribution to it from any specified velocity $V$ and any specified scattering angle. In other words, similar rules hold for the integral and differential cross sections (§ 3.1). Then, the distribution function for $V$ in Eq. (1) need not be Maxwellian.

6. These results apply also to the collisions in which a vibronic (vibrational-electronic) transition occurs simultaneously with the rotational transitions (§ 3.1).

7. The results are valid for pumping by any particle with or without internal structure (§ 3.1), except for the case explained in item 8.

8. The sudden approximation breaks down for purely rotational transitions of dipolar molecules in collisions with charged particles at small scattering angles. A modified theory shows that the pumping rate for a linear dipolar rotator depends on $J'$ even in the approximation that $\exp(-E_r/kT_r) \approx 1$ (§ 3.2).

From the generality of the results of this paper, the author expects their usefulness for interpreting many of the data on abnormal or maser emission that have been observed to data and that will be detected in the future.

§ 2. Consequences of a slow-rotation approximation to the pumping collisions

Throughout this section we shall assume that the rotational motion of the maser molecule is much slower than the relative motion between the collision partners. To be specific, (A) the energy-sudden approximation with respect to the rotational motion will be made for the scattering amplitude for the pumping collision (cf. the Appendix). In §§ 2.1~2.5 we shall also assume (B) that the velocity $V_r$ of the relative motion in the final channel is independent of the rotational channels $(I', I'')$. In § 2.6, however, this assumption will be slightly relaxed; we shall assume (B') that $V_r$ depends only little on $(I', I'')$.

2.1. Collisional pumping rate from the principle of detailed balance
We shall use the principle of detailed balance

\[ g_L K(v'\Gamma''\leftarrow v\Gamma'; T) = g_R K(v''\Gamma\leftarrow v\Gamma; T) \]  \hspace{1cm} (4)

for the rotational degrees of freedom. Equation (4) follows from assumptions (A) and (B) (cf. the Appendix); according to assumption (B) the rotational energy difference \((\Delta E)_{\Gamma'\Gamma} = E_{\Gamma'} - E_{\Gamma}\) has been neglected as compared with \(E\). Substitution of Eq. (4) into Eq. (3) gives an expression for the pumping rate

\[ P(v'\Gamma''\leftarrow v; T, T_r) = N_v N_p \sum_{\Gamma} \exp(-E_{\Gamma}/kT_r) K(v'\Gamma''\leftarrow v\Gamma; T) \]  \hspace{1cm} (5)

2.2. The rotational-invariance rule for linear rotators

Following Watson et al.\(^4\), we shall first consider pumping of linear rotators in a hot gas to a low-lying rotational state \(\Gamma\), and shall approximate the exponential factor in Eq. (5) by unity. Then, the sum over \(\Gamma\) reduces to a rotationally summed collision rate constant, i.e., to the Maxwellian average of the product of \(V\) and a rotationally summed cross section

\[ \sum_{\Gamma} \sigma(v' J''\leftarrow v J; E) \].

This sum is independent of \(J'\) on the assumptions (A) and (B).\(^{5,10\}\) Therefore, the collisional pumping rate is independent of \(J'\).

This argument is equivalent to Watson et al.'s derivation, and clarifies which physical consequences of the assumptions (A) and (B) justify the rotational-invariance rule, an important point that Watson et al. do not explicitly state. Thus the rule applies approximately to collisions that nearly satisfy the rotational sum rule and the principle of detailed balance (4), even if the scaling-relation formula, used by Watson et al., for the individual cross sections is invalid. Also, the argument in this subsection allows immediate but useful generalizations to be made in the rest of this paper.

2.3. Sum rules for the collision rate constants

A nonlinear polyatomic molecule may be represented, in a first approximation, by a rigid rotator having three principal moments of inertia \((I_a, I_b, I_c)\). If two of them are equal, just as for NH\(_3\), the rotator is a symmetric top and has a third quantum number \(K (0 \leq K \leq J)\) for the angular momentum about the body-fixed symmetry axis. The rotational states are degenerate in \(M\) just as for a linear rotator, and states with nonzero \(K\) are doubly degenerate; \(\Gamma\) denotes the set \((J, K)\).

A diatomic or a linear polyatomic molecule in a non-\(\Sigma\) state has a nonzero quantum number \(A\) for the projection of the electronic orbital angular momentum onto the molecular axis. Such a molecule may be regarded as a symmetric-top rotator having \(K\) equal to \(A\).
A spherical top is a special case of a symmetric top for which $I_a = I_b = I_c$. An example is the CH$_4$ molecule. The rotational states are degenerate in both $M$ and $K$. Thus, $\Gamma = J$ just as for a linear rotator.

The three principal moments of inertia are all different for an asymmetric-top rotator such as H$_2$O and H$_2$CO. The rotational levels of an asymmetric top are degenerate in $M$. They are often denoted by $J_r$, $\tau$ being an index running from $-J$ to $J$. Another popular notation is $J_{K_1,K_2}$, the subscripts indicating $K$ for the limiting prolate-symmetric-top state and the limiting oblate-symmetric-top state that the asymmetric-top state approaches continuously when the moments of inertia change continuously. $\Gamma$ may be either $(J, \tau)$ or $(J, K_1, K_2)$.

With this understanding of $\Gamma$, we define moments of the collision rate constant with respect to $(\Delta E)_{rr'} (= E_r - E_{r'})$ by

$$S_n(T_g; \Gamma') = \sum_{r'}(\Delta E)_{rr'} K(v'\Gamma' \leftrightarrow v\Gamma''; T_g).$$

(6)

On the assumptions (A) and (B) the moments $S_n(T_g; \Gamma')$ and $S_1(T_g; \Gamma')$ for a linear, spherical-top, symmetric-top or asymmetric-top rotator are independent of $\Gamma'$, and hence, may be replaced by the moments $S_n(T_g; 0)$ and $S_1(T_g; 0)$ for the ground rotational state; see Ref. 11) for a proof without the use of a scaling-relation formula. These ground-state moments, hereafter denoted simply by $S_0(T_g)$ and $S_1(T_g)$ without the parameter 0 for $\Gamma'$, are much easier to calculate than $S_n(T_g; \Gamma')$ for a general $\Gamma'$.

2.4. Rotational-invariance rule for nonlinear rotators

The rotational-invariance rule in § 2.2 for a linear rotator can now be readily generalized for spherical-top, symmetric-top and asymmetric-top rotors. Consider pumping to a low-lying rotational state $\Gamma'$ and replace the exponential factor in Eq. (5) by unity. Then, it follows from the $\Gamma'$-independence theorem for $S_0(T_g; \Gamma')$ that

$$P(v'\Gamma' \leftrightarrow v; T_g, T_r) = N_p N_v S_0(T_g),$$

(7)

which is indeed independent of $\Gamma'$.

2.5. Dependence on the rotational state

For high-lying rotational states, the exponential factor in Eq. (5) deviates from unity. Writing this factor as a product

$$\exp(-E_{r'}/kT_r)\exp[-(\Delta E)_{rr'}/kT_r]$$

and expanding the second factor in terms of its exponent, we have

$$P(v'\Gamma' \leftrightarrow v; T_g, T_r) = N_p N_v \exp(-E_{r'}/kT_r)$$
Because the rate constants are appreciable only for levels $\Gamma$ near $\Gamma'$, small values of $(\Delta E)_{rr'}$ dominate the moments $S_n(T_\theta, \Gamma')$. Therefore, the series in Eq. (8) converges rapidly, unless the rotational temperature is low. Neglect of the terms with $n > 2$ and use of the $\Gamma'$-independence theorem for the first two moments lead to an approximate expression

$$P(v' \Gamma' \rightarrow v; T_\theta, T_r) = N_p N_v \exp\left(-\frac{E_r}{k T_r}\right) \left(\frac{S_0(T_\theta) - \frac{S_1(T_\theta)}{k T_r}}{k T_r}\right)$$

for linear, spherical-top, symmetric-top and asymmetric-top rotators.

Equation (9) depends on $E_{r'}$ and on $T_r$ in a simple way. The quantities dependent on $T_\theta$ are independent of $T_r$, and vice versa. At high rotational temperatures and for a low-lying rotational state for which $E_{r'} < k T_r$, neglect of the second term recovers Eq. (7). Thus, Eq. (9) clearly indicates a criterion for the validity of the rotational invariance rule.

### 2.6. Correction for the kinematic factor

The assumption (B') shall now replace the assumption (B); we shall take approximate account of the rotational-channel dependence of the final-channel velocity $V_i$. We still make the sudden approximation for the scattering amplitude. In the calculation of the cross section from the scattering amplitude, however, we introduce the kinematic factor $V_i/V$ to the first order in $(\Delta E)_{rr'}$. This adds a correction term to the principle of detailed balance (4), as shown in Eqs. (A5) and (A6) in the Appendix. Then, we need to consider a moment

$$\bar{S}_1(T_\theta) = \sum_{r} (\Delta E)_{rr'} \bar{K}(v' \Gamma' \rightarrow v \Gamma'; T_\theta)$$

of the modified rate constant $\bar{K}$ of Eq. (A6). In the sudden approximation this moment is independent of $\Gamma'$ for the same reason as led to the $\Gamma'$-independence of $S_1(T_\theta; \Gamma'),^{11,12}$ and is calculable from the cross sections for transitions from the ground rotational state. After all, the kinematic factor modifies Eq. (9) to the lowest order in the rotational-channel dependence as

$$P(v' \Gamma' \rightarrow v; T_\theta, T_r) = N_p N_v \exp\left(-\frac{E_r}{k T_r}\right) \left(\frac{S_0(T_\theta) - \frac{S_1(T_\theta)}{k T_r}}{k T_r} + \bar{S}_1(T_\theta)\right).$$
Definition (A6) of $\bar{K}$ indicates that, if $kT_r \approx kT_s \gg (\Delta E)_{v'v}$, the last two terms in the large parentheses in Eq. (11) are of the same order. If $kT_r \approx kT_s \approx (\Delta E)_{v'v}$, then $\bar{S}_1(T_s)$ may even dominate over $S_1(T_s)/kT_r$.

§ 3. Discussion

3.1. Generality of the proof

The rotational-invariance rule (7) and the rotational-state-dependence formulas (9) and (11) have followed from two consequences of the assumptions (A) and (B) (or (A) and (B')), namely, $(a)$ the principle of detailed balance (4) (or (A5)) for the collision rate constants and $(b)$ the $I''$-independence theorem for $S_0(T_s; I'; I'')$, $S_1(T_s; I'')$, and $\bar{S}_1(T_s)$. The same assumptions lead to relations, similar to $(a)$ and $(b)$, for the cross sections, either integral or differential. Therefore, the results of the preceding section apply also to the differential and the integral cross sections, i.e., to the quantities inside the angle brackets that indicate an average over the Maxwellian distribution of $V$. In other words, Eqs. (7) and (9) for $P(v' \Gamma' \leftarrow v; T_s, T_r)$ remain equally valid, if, in definition (3) of $P(v' \Gamma' \leftarrow v; T_s, T_r)$ and in definition (6) of $S_0(T_s; I')$, the rate constants $K(T_s)$ are replaced by the integral cross sections $\sigma(E)$ or by the differential cross sections $d\sigma(E)/d\omega$. A similar statement applies to Eq. (11) with $\bar{S}_1(T_s)$ appropriately changed. In short, Eqs. (7), (9) and (11) are valid also for the individual contribution to the pumping rate from any specified scattering angle $\theta$ and any specified velocity $V$.

An immediate consequence of this observation is that the results of § 2 hold true for any velocity distribution function, i.e., even for non-Maxwellian distribution of $V$.

So far we have considered rotational-vibrational transitions within a specified vibrational transition $v' \leftarrow v$. That the transition $v' \leftarrow v$ is vibrational, however, has never appeared really in the derivation of $(a)$ or $(b)$ or in the arguments in the present paper. The results of the preceding section need no change, if an electronic transition accompanies the rotational-vibrational transitions. More generally, the index $v$ may be understood throughout this paper to specify a vibronic state, i.e., a coupled or uncoupled vibrational-electronic state, provided that the assumptions (A) and (B) (or (A) and (B')) are good.

We have paid attention only to the transitions of the maser molecule and not to those of the collision partner; indices $v$, $v'$, $\Gamma$ and $\Gamma'$ refer to the maser molecule. In effect, we have implicitly assumed the collision partner to have no internal structure. Rules $(a)$ and $(b)$ and the results of the present paper, however, remain equally valid, if the collision partner (CP) has any kind of internal degrees of freedom and makes a transition $n_{cp} \leftarrow n_{cp}$ of the internal state. In this case we have only to regard the index $v(v')$ as including the new index $n_{cp}$.
The collision partner also may be a molecule. Then the index \( n_{CP} \) may specify a rotational as well as a vibronic state of the collision partner. Its rotational motion may couple with the vibronic motion. Even then, Eqs. (7), (9) and (11) remain valid. Equation (9) or (7) can be summed over \( n_{CP} \) and averaged over \( n_{CP} \) (with any weight function) without change in the form of the equation, if we define the rate constants \( K \) in Eqs. (3) and (6) to have been summed over \( n_{CP} \) and averaged over \( n_{CP} \). (We may sum and average Eqs. (7) and (9) even over the vibronic states of the maser molecule.) Of course, the summation and average need not be over all states \( n_{CP} \) and all states \( n_{CP} \). For example, we may sum and average Eqs. (7) and (9) over only the rotational states, either all or only a few, of the collision partner. Note that the sudden approximation for the scattering amplitude has been made with respect only to the rotational motion of the maser molecule and to no internal motion of the collision partner. Watson et al.\(^4\) have recognized this for collisions between linear rotators on the basis of Launay's work.\(^13\)

### 3.2. Validity of the sudden approximation

The energy-sudden approximation (A) used in the derivation of Eqs. (7), (9) and (11) breaks down, if the effective collision time \( r_c \) is comparable to or longer than the rotational period \( r_{rot} \) of the maser molecule. Thus the following three cases need special consideration.

1. For collision energies \( E \) just above an excitation threshold \( \Delta E \) the effective collision time is long, because the relative motion is slow after the collision. Let \( a \) be the size of the effective interaction region and \( \mu/m_{H} \) the reduced mass of the collision system measured in units of the mass \( m_{H} \) of the hydrogen atom. The condition \( r_e \ll r_{rot} \) for the validity of assumption (A) is\(^14\)

\[
\frac{(E-\Delta E)}{E_{r'}} \geq 0.04 \times a(\text{Å})((\mu/m_{H})B(\text{cm}^{-1}))^{1/2},
\]

where \( B \) is the rotational constant if the molecule is a linear or a spherical-top rotator. For a symmetric or asymmetric top, a safe choice of \( B \) is the maximum rotational constant. A representative value of the collision energy \( E \) is of the order of \( kT_e \). The square of the left-hand side of inequality (12) must also be much larger than unity for assumption (B) to be good.

2. During collisions at energies in an extremely narrow resonance, the collision partners form a complex and stay close to each other for a long time. For assumption (A) to be valid, the width \( \Gamma_{res} \) of the resonance must satisfy an inequality\(^15\)

\[
2\Gamma_{res} \gg \sqrt{BkT_e}.
\]

Equations (7), (9) and (11) may be invalid, if a large contribution to the collision
rate constant comes from one or more narrow resonances violating inequality (13).

iii) Distant collisions between a charged particle and a molecule with a nonzero dipole moment $D$ can induce purely rotational transitions to a significant extent. Such collisions are dominated by the long-range dipole potential that decreases slowly as $\sim r^{-2}$ as the distance $r$ between the collision partners becomes large. Therefore, the effective interaction region is large and the effective collision time is long for small scattering angles $\theta$ that correspond to distant collisions. Indeed, assumption (A) breaks down for forward scattering of a charged particle by a dipolar molecule, giving a divergent differential cross section for purely rotational transitions at $\theta = 0$ at any collision energy. For this reason the integral cross section and the collision rate constant diverge if $v' = v$, and so does the collisional pumping rate as defined by Eq. (3).

Consider collision energies $E$ that are sufficiently above the thresholds for excitation of the relevant rotational levels. Then, the sudden approximation should be good for most collisions. For the distant collisions for which the assumption (A) is invalid, the interaction between a dipolar molecule and a particle with a charge $ze$ ($-e$ being the charge of an electron) is weak and acts as a small perturbation. There must be scattering angles $\theta_c$ such that assumptions (A) and (B) are good for $\theta \geq \theta_c$ and that the first Born approximation with only the dipole potential taken into account is accurate for $\theta \leq \theta_c$. If we switch from the sudden approximation to the first Born approximation at any one of such values of $\theta_c$, the integral cross sections for the pure rotational transitions of a linear dipolar rotator satisfy

$$\sum_{J} \sigma(vJ \rightarrow vJ'; E) \approx \sum_{J} \sigma(vJ \rightarrow v0; E) - A(J') \frac{8\pi}{3} \left( \frac{zeD}{Vh} \right)^2$$

(14)

with

$$A(0) = 0$$

and

$$A(J') = \frac{1}{2J'+1} \{ (J'+1) \ln(J'+1) + J' \ln J' \}. \quad (J' \geq 1)$$

(15)

Note that $\theta_c$ is absent from Eq. (14). Multiplications of both sides of Eq. (14) by $V$ and averages over the Maxwellian distribution of $V$ lead to $S_0( T_k; J')$ dependent on $J'$:

$$S_0( T_k; J') = S_0( T_k) - 1.53 \times 10^{-4} \text{ cm}^3 \text{ s}^{-1} \times A(J') \sqrt{\frac{\mu J}{m_u}} T_k(\text{K}) \{ zD(\text{debye}) \}^2.$$
This equation should replace $S_0(T_\ast)$ of Eqs. (7) and (9), leading to a pumping rate dependent on $J'$ even in the approximation that $\exp(-E_r/kT_r) \approx 1$. Similarly, $S_1(T_\ast)$ in Eq. (9) also needs modification, which will not be explicitly written here, because Eqs. (14) and (16) neglect a small term of the same order as $S_1(T_\ast)$.

Finally, four remarks are due on Eq. (16). First, the pumping rate decreases with increasing $J'$ because of the second term of Eq. (16). This term arises from a part of the rotational transitions with $J-J' = \pm 1$. Second, the region of $T_\ast$ in which Eq. (16) is applicable is larger for pumping by light particles, such as electrons or positrons, than for pumping by ions. Third, the sum $S_0(T_\ast; J')$ includes, by definition, the elastic process, which contributes nothing to pumping. In subtracting the elastic rate constant from $S_0(T_\ast; J')$ one may use a scaling relation involving the Clebsch-Gordan coefficients $C(J', 2j, J'; 000)$:

$$K(vJ' \leftarrow vJ) - K(v0 \leftarrow v0) = \sum_{j'=1}^{J'} (C(J', 2j, J'; 000))^2 K(v, 2j \leftarrow v0).$$

(17)

Contributions from small $j$ dominate the sum. Fourth, the pumping rate per collision can be larger for electron-molecule collisions than for atom-molecule or molecule-molecule collisions by many orders of magnitude, if the molecule is dipolar. Depending on the electron density and on the gas temperature, electron collisions can play an appreciable role in pumping molecules with a large dipole moment or in effecting an abnormal emission from them.

**Appendix**

--- The Energy Factor in the Principle of Detailed Balance ---

Consider rotational-vibrational or rotational-vibronic transitions in particle-molecule collisions. The initial (final) molecular wave function is approximated by the product of a vibronic wave function and a wave function of a general asymmetric-top rotator. The purpose of this appendix is to discuss the energy factor in the expression for the principle of detailed balance when the collision is sudden compared with the rotational period of the molecule.

Let $M_r$ specify a sublevel of a rotational state $\Gamma$ of the molecule. (See §§ 1.2 and 2.3 for the meaning of $\Gamma$.) Consider a transition $v' \Gamma' M_{r'} \leftarrow v \Gamma M_r$, $v$ denoting a pair of a vibrational or vibronic state of the molecule and an internal state, if any, of the collision partner. The kinetic energy of the relative motion changes from $E$ to $E'$. We write the difference between them as the sum of the rotational-energy difference $(\Delta E)_{r' \rightarrow r}$ and the remainder:

$$E - E' = (\Delta E)_{v' \leftarrow v} + (\Delta E)_{r' \rightarrow r}.$$  

(A1)

Following Chase\(^9\) we define a scattering amplitude $F(v' \leftarrow v; \varepsilon)$ for a fictitious
collision in which the molecular orientation is held fixed during the collision. 
The collision energy $\varepsilon$ is equal to $E$ within an ambiguity of $\sim (\Delta E)_{r'r}$. The 
scattering amplitude $f_{SA}$ in the sudden approximation is \(^9\)

$$f_{SA}(v' \Gamma' M_{r'} \leftarrow v \Gamma M_r; \varepsilon) = (\Gamma' M_{r'} | F(v' \leftarrow v; \varepsilon) | \Gamma M_r). \quad (A2)$$

The differential cross section from Eq. (A2), when summed over $M_r$ and $M_{r'}$ and 
divided by the number $g_r$ of the degenerate initial states, leads to the degeneracy-
averaged differential cross section

$$\frac{d\sigma_{SA}}{d\omega}(v' \Gamma' E' \leftarrow v \Gamma E) = \frac{1}{g_r} \left( \frac{E'}{E} \right)^{1/2} \sum_{M_r M_{r'}} |f_{SA}|^2. \quad (A3)$$

An interchange of $(\Gamma', M_{r'})$ and $(\Gamma'', M_{r''})$ changes, in general, the squared 
scattering amplitude $|f_{SA}|^2$, but does not change its sum in Eq. (A3). Therefore, 
neglect of the energy factor $(E'/E)^{1/2}$ results in the principle of detailed balance  
(4) in the text. Our aim here, however, is to study the role of the energy factor.

Consider two different rotational transitions occurring at the same collision 
energy $E$; after the transition $v' \Gamma' \leftarrow v \Gamma$ the energy of the relative motion is the 
$E'$ of Eq. (A1), and after the transition $v' \Gamma \leftarrow v \Gamma'$ it is $E - (\Delta E)_{v'v} + (\Delta E)_{r'r}$. 
Note that, for purely rotational transitions ($v' = v$), the usual principle of detailed 
balance connects cross sections for the processes $(\Gamma'' E'' \leftarrow \Gamma E)$ and $(\Gamma E' \leftarrow \Gamma' E')$, 
while our interest is now in the connection between the processes $(\Gamma' E'' \leftarrow \Gamma E)$ and 
$(\Gamma E' \leftarrow \Gamma' E)$. The latter connection is more useful, when different transitions 
occur in the same environment, as is the case with the situation considered in the 
text. It follows from Eq. (A3) that

$$g_r \frac{d\sigma_{SA}}{d\omega}(v' \Gamma' \leftarrow v \Gamma; E) \approx g_r \left( 1 - \frac{(\Delta E)_{r'r}}{E - (\Delta E)_{v'v}} \right) \frac{d\sigma_{SA}}{d\omega}(v' \Gamma \leftarrow v \Gamma'; E) \quad (A4)$$

to the first order in $(\Delta E)_{r'r}$. Because the collision energy is the same on both 
sides, Eq. (A4) may be averaged over any distribution of $E$ after multiplication 
by the velocity $V$ that corresponds to the energy $E$; we obtain a relation between 
the rate constants $K$ for the two transitions as

$$g_r K(v' \Gamma' \leftarrow v \Gamma) \approx g_r K(v' \Gamma \leftarrow v \Gamma') - g_r (\Delta E)_{r'r} \bar{K}(v' \Gamma' \leftarrow v \Gamma'') \quad (A5)$$

with

$$\bar{K}(v' \Gamma' \leftarrow v \Gamma'') \equiv \langle V \cdot \sigma(v' \Gamma' \leftarrow v \Gamma''; E) / (E - (\Delta E)_{v'v}) \rangle. \quad (A6)$$

On the assumption (B) in § 2 the term involving $(\Delta E)_{r'r}$ is negligible (cf. Eq. (4)). 
On the assumption (B'), however, this term should be and is retained in § 2.6.
I. Shimamura

References

7) I. Shimamura, Res. Note ISAS RN83 (Institute of Space and Aeronautical Science, University of Tokyo, Apr. 1979).
14) I. Shimamura, to be published.