ROTATIONAL EXCITATION OF INTERSTELLAR OH MOLECULES*

R. KOSLOFF, A. KAFRI, AND R. D. LEVIN

Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel

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ABSTRACT

The relative rates for exciting rotational states of OH in collisions with H (or H₂) at low temperatures are estimated. It is found that these rates are dominated by the statistical (phase space) factors which favor the production of the lowest rotationally excited states of OH. The required conditions for collisional pumping of the OH 1720 MHz emission line are thus satisfied.

Subject headings: interstellar: molecules — molecular processes

I. INTRODUCTION

Inversion of the 1720 MHz line of OH (Elitzur 1976, 1977 and references therein) can be understood provided that collisional excitation of the ground \( ^2\Pi_{3/2}(J = 3/2) \) state significantly populates the lowest excited rotational state \(^2\Pi_{3/2}(J = 5/2)\). For a closed-shell molecule such behavior is to be expected. The rate of excitation of any single quantum state is typically found to be a decreasing function of the excitation energy. Analysis (Levine et al. 1976; Proccacia and Levine 1976a, b, c) shows that there are two contributing factors. One is the volume in phase space available to the final states. For rotational excitation in an atom-diatomic collision this volume decreases with increasing excitation energy (but is proportional to the degeneracy of the final rotational level). The second factor in the transition rate is dynamic in origin. (It is essentially the thermally averaged magnitude of the square of the appropriate \( S \)-matrix element.) The dynamic constraints reflect the forces operating during the collision. For low-energy rotational excitation it is found (Proccacia and Levine 1976a, b, c) that the dynamic factor reflects the inertia of the rotational angular momentum of the molecule (Kafri and Kosloff 1977). Transitions involving the least change in the rotational state are thus also preferred on dynamical grounds.

OH (and other open-shell diatomic molecules) offer a possible exception to these general considerations. For such molecules there will be an additional low-lying manifold of rotational states, as shown (in a simplified fashion) for OH in Figure 1. The existence of this second manifold opens the possibility of low-energy transitions which require no change on the \( J \) quantum number of OH. On the other hand, the kinetic energy of the collision partners will change during such transitions. They will thus be constrained by the dynamic inertia of the linear momentum (Kafri et al. 1975). The existence of the second low-lying manifold of rotational states implies that a compromise must be achieved between the tendency of the molecule to conserve its linear and its angular momentum during the collision. The changes in the linear and the angular momentum cannot simultaneously be small.

The purpose of the present paper is to assess the relative importance of the two dynamical inertia in low-energy \( H + OH \) collisions. Special reference is made to transitions out of the ground state. It is concluded that because of the low mass of \( H \) (or of \( H_2 \)) the torque that is imparted during the collision is small (in units of \( \hbar \)). The dynamic inertia indeed disfavors large \( J \) (or \( M_J \)) transitions as compared to changes in the linear momentum which require comparable excitation energy. Even so, for realistic intermolecular forces and anisotropies the angular inertia is found to be large but not dominant.

An additional factor that must be considered is the volume in phase space available for the different final states. At low temperatures this last factor completely overshadows the role of the dynamical constraints. Representative results are shown in Figure 2. For all reasonable estimates of the dynamical constraints we find that the rate of the "iso-J" transition \( (^2\Pi_{3/2}(J = 3/2) \rightarrow ^2\Pi_{1/2}(J = 3/2)) \) does not particularly exceed the rate of production of the lowest excited rotational state \(^2\Pi_{3/2}(J = 5/2)\). Only by an artificial enhancement of the rotational inertia could we make the "iso-J" transitions to be the dominant one. Even then, the effect was limited to higher temperatures (say \( T > 200 \) K), and the \(^2\Pi_{3/2}(J = 3/2) \rightarrow ^2\Pi_{3/2}(J = 5/2) \) transitions remained quite probable. We conclude that the conditions required for collisional pumping of the OH 1720 MHz line are readily satisfied.

The information-theoretic methods employed in this study (Levine 1973; Bernstein and Levine 1975) have not yet reached a maturity comparable to that of a direct dynamical method (e.g., a numerical solution of the equations of motion; see, for example, Green 1975 or Chu 1976). Even so, these methods have been extensively compared with both computational and experimental studies of rotational energy transfer and of other molecular processes, and have already been subject to several predictive tests.

The information theoretic method we employ is discussed in § II. Particular attention is given to the novel

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feature of the analysis, i.e., the presence of two dynamic constraints of conflicting roles. An analytic expression for the phase-space factor is also provided. Results for the low temperature rotational excitation of OH are discussed in § III. A comparison of the present conclusions with the results obtained for closed-shell molecules, additional applications of the present method, and a summary are provided in § IV.

II. INFORMATION THEORY

a) The Prior Rate

In the information-theoretic approach (Levine 1973; Bernstein and Levine 1975) the actual rate is represented in terms of its deviation from a “prior” rate. The prior rate obtains when there are no dynamic constraints so that

![Figure 2](image-url)

Fig. 2.—Temperature dependence of the rates for $^3\Pi_{2p}(J = 3/2) \rightarrow ^3\Pi_{2p} (J')$ transitions relative to the rate of the $^3\Pi_{2p}(J = 3/2) \rightarrow ^3\Pi_{2p} (J' = 5/2)$ transition. (a) The prior rates (when all final quantum states are equally probable). (b) Rates computed using the most reasonable parameters ($\lambda \Delta E_0 = 0.625, \langle \Delta \beta^2 \rangle^{1/2} = 0.3 \sigma_0, \langle \beta^2 \rangle = 6 \sigma_0^2$). (c) Rates computed using extreme values of the parameters (which border on the unphysical, $\lambda \Delta E_0 = 0.312, \langle \Delta \beta^2 \rangle^{1/2} = 0.07 \sigma_0, \langle \beta^2 \rangle = 1 \sigma_0^2$). The introduction of the dynamic constraints definitely enhances the relative rates for transitions into the low-lying states of the $^3\Pi_{1/2}$ manifold, but unrealistic magnitudes (case c) are required for these rates to dominate.
all final quantum states are equally probable. The probability of any final level is thus proportional to the volume in phase space available to the collision products. At a given total energy \( E \) the rate of any \( x(J) \rightarrow y(J') \) transition is explicitly given by

\[
k^2(x(J) \rightarrow y(J'); E) = R g_x g_y (2J' + 1) \rho_x(E_x).
\]

(1)

Here \( \rho_x(E_x) \) is the density of final translational states (\( \rho_x(E_x) = A_x E_x^{-1/2} \), \( A_x = \mu^{3/2} / 2^{1/2} \pi^{3/2} \), \( \mu \) the reduced mass) at the initial kinetic energy \( E_x \). \( 2J' + 1 \) is the degeneracy of the rotational level \( J' \), \( g_x \) is the degeneracy of the nuclear spin states, and \( g_y \) is the electronic degeneracy of the \( y \) manifold of rotational levels. \( R \) is a proportionality constant which is taken to be energy independent.

The rate at a (translational) temperature \( T \) is given by averaging (1) over a Boltzmann distribution in the initial translational energy, \( E_x = (E_x/2\pi kT)^{1/2} \) is the translational partition function, and \( k \) is Boltzmann's constant). The integration is analytic (the general algorithm for all possible prior rates is given in Levine and Manz 1975) and leads to

\[
k^2(x(J) \rightarrow y(J'); T) = (4\pi \hbar kT) Q_x Q_y g_x g_y (2J' + 1) \Delta \exp \Delta K_1(\Delta).
\]

(2)

\( K_1(\Delta) \) is the modified Bessel function of the first order, and \( \Delta \) is the "reduced" energy transfer:

\[
\Delta = [E_{x(J)} - E_{y(J')}] / 2kT.
\]

(3)

For negative values of \( \Delta \) (i.e., for excitation processes) we define \( K_1(\Delta) \) by the condition \( -\Delta K_1(\Delta) = \Delta K_1(\Delta) \).

Three factors are evident in the result (2) for the prior rates. The first, \( A_x(T) = (4\pi \hbar kT) Q_x Q_y \), is due to the transla-
tional motion and is common to all final states. The identity of the atom with which the diatom collides enters only through this factor. The second factor is the degeneracy, \( g_x g_y (2J' + 1) \), of the final level \( y(J') \). The third factor is the rate into a single final quantum state, \( A_y(T) \Delta \exp \Delta K_1(\Delta) \), obtained by dividing the rate into the level \( y(J') \) by the number of states in the level. It follows from the properties of the modified Bessel function that the rate into a single final state is a monotonically increasing function of the reduced energy transfer \( \Delta \). It is important to note that for excitation processes, where \( \Delta \) is negative, this implies that the prior rate decrease as the internal energy of the final states increases. Explicitly, for excitation processes (\( \Delta \leq 0 \)) we obtain, as \( -\Delta \rightarrow \infty \),

\[
k^2(x(J) \rightarrow y(J'); T) = g_x g_y (2J' + 1) \Delta^{1/2} A_y(T) \exp(-2\Delta).
\]

(4)

and, as \( \Delta \rightarrow 0 \),

\[
k^2(x(J) \rightarrow y(J'); T) \rightarrow g_x g_y (2J' + 1) \Delta A_y(T).
\]

(5)

At low temperatures the prior rate is thus indeed dominated by the "Boltzmann" factor \( \exp(-2\Delta) \). As argued by Elitzur (1976), this Boltzmann factor favors the least possible energy transfer and hence discriminates in favor of the production of the lowest excited state. The analytic expression (2) enables us, however, to examine the importance of the phase-space volume at all temperatures. As \( \Delta \rightarrow 0 (T \rightarrow \infty) \), it is only the degeneracy of the final level that determines the rate.

b) Dynamic Constraints

The prior rates obtain when (at a given total energy) all final quantum states are equally probable. Dynamic constraints tend to differentiate among the possible final states; some transitions are found to be significantly more probable than others. There is in fact a profusion of propensity rules for different processes (for molecular collisions see, for example, Levine and Bernstein 1974). In the information-theoretic approach the dynamic constraints are included by seeking a set of transition probabilities which satisfy the quantitative relations required by the dynamic constraints and which otherwise least discriminate between the final quantum states. The advantage of this procedure is that one can proceed in a single step from the dynamical constraint to an explicit expression for the relative rates. No additional assumptions beyond the identification of the dynamic constraints are required. An explicit demonstration of the procedure will be provided below, in §1c.

To identify the dynamic constraints in the H + OH collision, we have simplified the internal structure of OH to that shown in Figure 1. Specifically, in the present study we are neglecting the dynamic constraints associated with the A-doubling (Ottinger, Velasco, and Zare 1970; Gwinn et al. 1973). An understanding of the inversion in interstellar CH (Elitzur 1977) along the present lines will thus require an additional dynamical constraint which we do not include. In the present study OH is a rotor characterized by a (half integer) angular momentum quantum number \( J \).

The conserved angular momentum, \( J \), in the collision is the vector sum of \( J \) and the orbital angular momentum \( L \), \( J = L + J = L' + J' \). The primes designate the variables of the final state. The changes in \( L \) and in \( J \) are thus perfectly anticorrelated, \( \Delta L = -\Delta J \). The second variable we consider is \( t \), \( t = p - p' \), (the linear) momentum transfer during the collision. The average \( \langle \Delta L \rangle \), of \( \Delta L \) over all final states of a given magnitude of \( t \) vanishes by symmetry,

\[
given t: \langle \Delta J \rangle = \langle \Delta L \rangle = 0.
\]

(6)
The second moment, \( \langle \Delta L^2 \rangle \), need not vanish. To evaluate it we introduce the impact parameter \( b \), \( L = b \times p \), and neglect the correlation between \( b' \) and \( p' \) so that

\[
given t: \langle \Delta L^2 \rangle = \langle (b \times p - b' \times p')^2 \rangle \approx \langle (b - b')^2 \rangle pp' + \langle b^2 \rangle (p' - p)^2.
\]  

(7)

Here \( \langle b^2 \rangle = \langle b'^2 \rangle \); and in obtaining (7) we have also invoked microscopic reversibility in the form \( p^2 \langle b^2 \rangle = p'^2 \langle b'^2 \rangle \). As a check one readily verifies that \( \langle \Delta L^2 \rangle \) is symmetric in the initial and final variables. In terms of translation energies, \( E_T = p^2/2\mu \) and \( T = t^2/2\mu \),

\[
given t: \langle \Delta J^2 \rangle = \langle \Delta L^2 \rangle = a(E_T E_T)^{1/2} + cT, \tag{8}
\]

where \( a = 2\mu \langle b^2 \rangle \) and \( c = 2\mu \langle b^2 \rangle \).

The condition \( \langle \Delta J \rangle = 0 \) implies that \( \langle \Delta J^2 \rangle \) is the “width” of the final, \( J' \), distribution about the initial \( J \). We thus expect that \( 1/\langle \Delta J^2 \rangle \) would be a measure of the inertia of the rotational momentum during the collision.

It is also to be noted that putting the constraint on \( \Delta J \) imposes a strong correlation between the initial and final projections of \( J \). The reorientation of \( J \) is thus constrained and, for a given initial \( m_J \), the final, \( m_{J'} \), distribution will not be statistical. If, however, the initial \( m_J \) distribution is statistical (i.e., one is computing the “degeneracy averaged” cross section), then the final \( m_{J'} \) distribution will also be statistical.

The dynamic constraints on the transfer of linear momentum have been previously discussed (Kafri et al. 1975). For collisions which involve no rearrangements these are

\[
\langle t \rangle = 0 \quad \text{and} \quad \langle t^2 \rangle = \frac{1}{2}\gamma \tag{9}
\]

where \( \gamma \) can be related to the “force” along the relative coordinate during the collision and the average is over all final states.

c) The Distribution of Minimal Information Content

The probability of any final \( y(J') \) state is defined in terms of the relative rate

\[
P[y(J')|x(J)] = \frac{k[x(J) \rightarrow y(J')]}{\sum k[x(J) \rightarrow y(J')]}, \tag{10}
\]

where the summation in the denominator is over all possible transitions. The prior probability is similarly defined in terms of the prior rates. In the information-theoretic approach the probabilities are determined by seeking to minimize the (nonnegative) information content \( I \),

\[
I = \sum P[y(J')|x(J)] \ln \{P[y(J')|x(J)]/P^o[y(J')|x(J)]\}, \tag{11}
\]

subject to the conditions that the probabilities are normalized and satisfy the dynamic constraints. The summation in (11) is over all final states, and the superscript \( o \) denotes the prior probabilities.

For the problem at hand where the dynamic constraint on \( \langle \Delta J^2 \rangle \) is at a given value of the momentum transfer \( t \) it is convenient to resolve the probability as

\[
P[y(J')|x(J)] = P[y(J')|t, x(J)]P[t|x(J)], \tag{12}
\]

Here \( P[t|x(J)] \) is the probability of a momentum transfer \( t \) for a given initial state while \( P[y(J')|t, x(J)] \) is the probability of the final state \( y(J') \) for a given momentum transfer and a given initial state. A similar resolution applies to the prior probabilities.

The technique of Lagrange multipliers, using (11) and the dynamical constraints (6), (7), and (9), provides (Kafri 1976; Kafri and Kosloff 1977),

\[
P[t|x(J)] = P^o(E_T) \exp (-\gamma t^2 - \gamma_0) = P^o(E_T) \exp (-\lambda T^2 - \gamma_0), \tag{13}
\]

where \( \lambda = 2\mu \gamma \) and \( \gamma_0 \) ensures that the distribution is normalized; and

\[
P[y(J')|t, x(J)] = \sum_{K=0}^{+\infty} \frac{(2K + 1) \exp [-\alpha(K + 1) - \gamma_0]}{(2\pi)^{1/2} \exp [-\alpha K(K + 1) - \gamma_0]}, \tag{14}
\]

where \( \alpha \) ensures that the distribution is normalized and \( \alpha = 1/(2\langle \Delta J^2 \rangle) \). In the classical limit where summation over \( K \) can be replaced by integration,

\[
P[y(J')|t, x(J)] = P^o[y(J')|t] \exp [-\alpha (J - J')^2 - \gamma_0] \tag{15}
\]

and

\[
P[y(J')|x(J)] = P^o[y(J')|x(J)] \exp [-\gamma t^2 - \alpha (J - J')^2 - (\alpha_0 + \gamma_0)]. \tag{16}
\]
When the range of $K$ is limited (as is the case in § III), the replacement of the summation in (14) by an integration is not warranted and should not be used.

From (10) and (1) the prior final state distribution (at a given total energy) is

$$P^s[y(J')|x(J)] = g_{y}g_{r}(2J' + 1)A_{y}E_{t}^{-1/2} \sum g_{y}g_{r}(2J' + 1)A_{r}E_{t}^{-1/2},$$

where the summation in the denominator is over all final states allowed by conservation of energy.

The actual rates are obtained from (10) as

$$k[x(J) \rightarrow y(J')] = k[x(J)]P[y(J')|x(J)].$$

Here $k[x(J)]$ is the rate of collisions of the initial state and is independent of the final state. The relative rates into different final states are thus completely specified by (16).

The result (16) provides a quantitative measure of the two conflicting dynamic constraints. The linear momentum transfer term favors the least possible $t$ which can be achieved by preferentially populating the very lowest excited states [i.e., $^2\Pi_{y=1/2}(J = 5/2)$ and $^2\Pi_{y=1/2}(J = 1/2)$, Fig. 1]. The angular momentum transfer term favors the least possible $\Delta J$, which can be achieved for the "iso-$J$" [to $^2\Pi_{y=1/2}(J = 3/2)$] transition. The relative importance of the two effects is measured by $g_{y}(\mu_{J}B_{t})$, where $B_{t}$ is the rotational constant.

Within the $^2\Pi_{y=1/2}$ manifold of rotational states the two terms in (16) operate in essentially the same direction. This is easily seen by noting that for transitions within the same manifold $t$ and $\Delta J$ are, approximately, the same variables. Thus, since $E_{t}^{L} + E_{t}^{R} = E_{t}^{L} + E_{t}^{R},$

$$t = (2\mu)^{1/2}(E_{t}^{L} - E_{t}^{R}) \approx (2\mu)^{1/2}(E_{t}^{L} - E_{t}^{R}) \approx (2\mu)^{1/2}(E_{t}^{L} - E_{t}^{R}) \approx 2\mu B_{t}^{1/2}(J' - J).$$

This is the situation for closed shell molecules where, at low energies, a single term in the exponent of (16) suffices. At high collision energies, the approximation in (16) deteriorate and both terms in (16) need to be explicitly present.

III. APPLICATIONS TO H + OH COLLISIONS

Relative rate constants for the $x(J) \rightarrow y(J')$ transition at the total energy $E$ can be obtained from the representation

$$k[x(J) \rightarrow y(J'); E] = k[x(J) \rightarrow y(J'); E][P[y(J')|x(J)]P[y(J')|x(J)]]^{-1}.$$

The transition probability is given by (12), (13), and (14), where the quantal distribution (14) was employed due to the large rotational constant ($B_{t} = 18.515$ cm$^{-1}$) of OH. Rate constants at a given temperature were obtained from (20) by a (numerical) averaging over a Boltzmann distribution of $E_{t}$ (except for the prior limit, $P = P_{x}$, where the integration is analytic, cf. § IIIa).

Three parameters enter the specification of the transition probabilities, $\lambda = 2\mu v$ (eq. [9]) and $a$ and $c$ (eq. [8]). Methods for estimating these parameters are available. (See, for example, Procaccia and Levine 1976a, b, c, or Koslow, Kafri, and Levine 1977). Rather than opt for a particular estimate, we have allowed a wide variation, over the reasonable range, as follows. The quantity $\lambda E_{t}$ was varied from 0.6 to 2, where $\lambda E_{t}$ is the energy difference between the two rotational manifolds. The quantity $ab_{t} = \mu(\Delta b^{2})/mr_{0}^{2}$ where $b_{t} = 1/(2mr_{0}^{2})$ and $r_{0}$ is the equilibrium distance of OH. Hence $[\langle \Delta b^{2}/r_{0}^{2} \rangle]^{1/2}$ was varied from 0.7 to 0.5. The quantity $c_{B_{t}} = \mu(\Delta b^{2}/r_{0}^{2})^{2}$; hence $[\langle \Delta b^{2}/r_{0}^{2} \rangle]^{1/2}$ was varied from 1 to 20. It should be noted in this connection that $r_{0}$ is essentially the inelastic cross section in units of the geometrical cross section $\pi r_{0}^{2}$ and that $[\langle \Delta b^{2}/r_{0}^{2} \rangle]^{1/2}$ is the range of changes in the impact parameter due to the transfer of angular momentum.

For almost the entire range of the parameters the temperature dependence of the relative rates was essentially governed by the prior rates. For transitions into the $^2\Pi_{y=1/2}$ manifold there is a steep rise at low temperatures (recall that for $^2\Pi_{y=1/2}(J = 3/2) \rightarrow ^2\Pi_{y=1/2}$ transitions $\Delta \geq -250/kT$ and note eq. (4)). As $[\Delta]$ decreases, the relative rates are being increasingly governed by the rotational degeneracy (2$J$ + 1) of the final level. Hence, as $T$ increases, final states of large $J'$ which are improbable at low $T$'s due to their large $[\Delta]'$s are becoming increasingly more probable. The "crossing" of the different rates as a function of $T$ seen in Figure 2 reflects the competition between the volume in phase space of the translational motion (which disfavors high $J$'s) and the number of quantum states that correspond to a particular $J'$ (which favors high $J$'s).

Only in the limit of a rather low $\lambda E_{t}$ (i.e., a wide spread in $E_{t}$) or a low resistance to changes in the linear momentum) and a rather high $a$ (a very small $ab_{t}$, i.e. very limited changes in $b$ and a very small $c_{B_{t}}$, i.e., a very small inelastic cross section) does the rate of the "iso-$J$" transition dominate. We do not consider the required combination of conditions [a very central (isotropic) and stiff H-OH potential] to be physically realistic. Even under such extreme conditions the rate of the "iso-$J$" transition dominates only at the higher temperatures (say $T > 75$ K) and by less than an order of magnitude at the temperature range ($T < 300$ K) studied.

We conclude that for H + OH collisions a very low propensity for changes in $J$ is required before the "iso-$J$" transition will dominate. It is interesting to note that for any other collision partner the "iso-$J$" transition will be maintained by a combination of conditions where the "iso-$J" transition is usually the most important.
even less likely. The effect is primarily through the dependence on the reduced mass. With any other atom, the reduced mass $\mu$ will be higher. Thus, for a Ne + OH collision, at the same value of $\langle \Delta b^2 \rangle / r_i^2$, $aB_1$ is some 10 times higher than for H + OH. For H$_2$ + OH the increase of $aB_1$ is about twofold. In addition, moreover, with the heavier partners the range of the intermolecular force is likely to increase.

IV. CONCLUDING REMARKS

The competition between the propensity to conserve angular momentum and the propensity to conserve linear momentum has been examined in general and with special reference to H + OH collisions. It was found that at low temperatures these dynamical effects are masked by the restrictions imposed by the volume in phase space that is available to the products. Only at the higher temperatures, where the energy transfer is already less than $kT$, does the role of the dynamic constraints become manifest. For OH, the considerable (270k) excitation energy of the "iso-J" transition makes it very unlikely that it will be overwhelmingly favored by the dynamics. CH, with an "iso-J" transition at about 72k, is a much more suitable candidate. On the other hand, collisions with H atoms are most likely to favor "iso-J" transitions. The reason is the low torque provided by the light H atom. Among all atoms, hydrogen is the least efficient for inducing changes in the rotational angular momentum of its partner. H$_2$ is about twice as efficient.

The central role of the products volume in phase space in determining the temperature dependence of the rates of excitation processes is similar to that found for rotational excitation of closed shell molecules (e.g., HD [Procaccia and Levine 1976a]). A similar behavior obtains for all endothermic processes (i.e., collisions where there is a decrease in the translational energy [Levine and Manz 1975]).

At higher energies a situation similar to that discussed here obtains also for closed-shell molecules. The additional rotational manifold is now the manifold of rotational states of the first excited vibrational level. Here as well one can discuss the relative efficiencies of the conversion of energy into (or out of) rotation and translation (Moore 1965). Application of the present method to such problems is well under way.

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R. KOSLOFF, A. KAFRI, AND R. D. LEVINE: Department of Physical Chemistry, The Hebrew University of Jerusalem, Givat Ram, Jerusalem, Israel

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