

## Resonances in recombination of atomic hydrogen due to long-range $H_3$ molecular states

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We present a calculation of the effective rate constant for three-body recombination, taking rearrangement into account. We find a pronounced resonance structure as a function of magnetic field due to long-range rovibrational states of  $H_3$  in an almost equilateral configuration. This structure is superposed on a rather flat background with a slow decrease below 10 T. The results are compared with experiment.

### I. INTRODUCTION

A vital and still unanswered question in the field of spin-polarized atomic hydrogen is the following: Will the finite lifetime due to collisional processes be longer than the time required for the establishment of the Bose condensed state? Theoretically this problem is far from settled and experimentally one has still not been able to reach a definitive conclusion, the present situation being that both the low- and high-density schemes, using traps<sup>1,2</sup> or compression of hydrogen bubbles,<sup>3</sup> respectively, are plagued by large decay rates.

However, to arrive at the Bose condensation regime, the density and hence the number of collisions per unit time may be kept at an acceptable minimum if one is able to cool the trapped atoms sufficiently or to affect directly the decay constants, which govern the time evolution of the system. The former goal may be achieved by using, for instance, evaporative<sup>1</sup> or laser (Lyman- $\alpha$ ) cooling,<sup>4</sup> whereas the rate constants can be manipulated by a variation of external parameters such as the detuning of a microwave trap<sup>5</sup> or the applied magnetic field.

The last possibility is especially suited for the high-density scheme and has stimulated the study of the three-body (dipolar) recombination process at very high field strengths both experimentally<sup>6</sup> as well as theoretically.<sup>7</sup> The first theoretical study<sup>8</sup> of the dipolar mechanism was a breakthrough in the understanding of the properties of doubly polarized atomic hydrogen gas at high densities. However, the analytic treatment showed a strong discrepancy with the experimental field dependence below 10 T. In view of the fact that the interest concentrates on values of the magnetic field for which the recombination rate is small, it is of importance to develop a more detailed picture of the recombination process. From the start, the role of spin-exchange taking place after the dipole transition was recognized as an important effect: the dipole-exchange mechanism.<sup>9</sup> This mechanism is contained in the  $f_2^d$  amplitude of Ref. 8, which was considered negligible in that investigation. An exact evaluation<sup>10</sup> of the  $f_1^d$  amplitude confirmed that this part

alone does not explain the recombination rate below 10 T. Also, a model which takes into account (in)elastic atom-molecule scattering with a fixed bound pair and symmetrizes afterwards was unsuccessful,<sup>7,10</sup> in agreement with the fact that dipole exchange can only be included by allowing all pairs to be bound. The most recent indication that such a model is indeed unsuccessful comes from a comparison of the above-mentioned experimental and theoretical work in Refs. 6 and 7.

In the present paper we present a calculation which includes dipole exchange in an approximate way. As we will show, this approach provides for a qualitative explanation of the slowly decreasing field dependence below 10 T and in addition suggests that the high rates found in recent high-field measurements may be due to a resonance effect caused by quasibound  $S = \frac{1}{2}$  states of the  $H_3$  molecule. In the picture we propose, the resonance effect enhances the dipole-exchange mechanism at certain values of the final atomic kinetic energy, i.e., at certain  $B$  values.

The paper is organized as follows. In Sec. II we indicate how the rearrangement channels can be included, extending our previous calculations<sup>10,7</sup> of (in)elastic atom-molecule scattering in such a way that all particle pairs are treated symmetrically from the beginning. In Sec. III A we give the results of the numerical evaluation of the model: We present the recombination rate constant in the magnetic field range 0–40 T and extract some information on the rovibrational relaxation of highly excited  $H_2$  molecules, which is of interest in its own right because it is to a large extent responsible for the undesirable heatup of the gas sample. The pronounced resonance structure which shows up in the decay rate is explained in Sec. III B in terms of quasibound rovibrational states of  $H_3$ . We end with some conclusions and suggestions for a better description of these states.

### II. RESONATING-GROUP THEORY

To make the paper self-contained and to set up a convenient notation, we briefly summarize some well-

known<sup>11,7</sup> facts about the bulk three-body recombination constant  $L_g$ . Two-body relaxation calculations<sup>12</sup> have shown that it is sufficiently accurate to treat the magnetic dipole interaction as a first-order perturbation. In addition, without the typical logarithmic energy dependence which prevails in two dimensions, and because the highest excited states of  $H_2$  have at least a binding energy of 70 K, the rate constant is expected to vary very slowly in the experimentally accessible temperature range of  $T < 1$  K. Hence it is permitted to take the zero-temperature limit.

Within the framework of these approximations  $L_g$  reduces essentially to a squared matrix element of the (electron-electron) magnetic dipole interaction between symmetrized initial and final states, denoted by  $|\mathcal{S}\Psi_f^{(+)}\rangle$  and  $|\mathcal{S}\Psi_f^{(-)}\rangle$ , respectively, summed over all possible final states. To aid physical insight we point out that the complex conjugated (i.e., time-reversed) configuration space wave function  $\mathcal{S}\Psi_f^{(-)*}$  describes an atom-molecule collision. In terms of single and double spin-flip (SF) processes the effective rate constant becomes

$$L_g^{\text{eff}}(B) = L_g^{1\text{SF}}(B) + 2L_g^{2\text{SF}}(B), \quad (1)$$

where we assume an additional recombination event on the helium surface after a double spin-flip process, because the outgoing atom will be in a  $|c\rangle$  state.

Both initial and final states are eigenstates of the Hamiltonian

$$H = H_0 + V, \quad (2)$$

which includes the central (singlet or triplet) interactions between the hydrogen atoms. Using the spectator-index notation<sup>13</sup> we write

$$V = \sum_{\alpha} V_{\alpha} \equiv V_{\alpha} + V^{\alpha} \quad (3)$$

and define the channel Hamiltonian

$$H_{\alpha} = H_0 + V_{\alpha}. \quad (4)$$

The operator  $H_0$  is the sum of the kinetic energies in the center-of-mass system and the Zeeman energies of the three atoms. Note that we neglect the possibility of a three-body force, which appears justified since in the initial state all particle pairs experience a strongly repulsive triplet interaction, while in the final state the molecular states involved turn out to be highly excited. In both cases at least one pair has a large separation. Furthermore, the influence of the hyperfine interaction is neglected in the final state, being a small higher-order effect.

In Refs. 9 and 10 we obtained the exact initial state  $|\mathcal{S}\Psi_i^{(+)}\rangle$  of three incoming spin-polarized hydrogen atoms, using the Faddeev formalism. Although this formalism is also applicable to the final atom-molecule state  $|\mathcal{S}\Psi_f^{(-)}\rangle$ , it is beyond the computational power of present supercomputers and we have to resort to an approximation. As a first step to a better understanding of the underlying reaction mechanism we formulated<sup>10,7</sup> a model in which (in)elastic scattering was taken into account but rearrangement was excluded, selecting one pair to be bound throughout the scattering process and symmetrized

ing afterwards. Here we present a formulation which is symmetrical in all pairs from the start and hence leads automatically to the inclusion of rearrangement (the dipole-exchange mechanism). The subtle differences between these two approaches will be made more explicit.

Resonating-group theory<sup>14</sup> is based on the variational principle

$$\langle \delta\Psi | E - H | \Psi \rangle = 0, \quad (5)$$

where  $|\delta\Psi\rangle$  and  $|\Psi\rangle$  are confined to a subspace of the total Hilbert space. The subspace to be used includes all possible open channels of atom-molecule scattering below the breakup threshold, with definite quantum numbers of total orbital angular momentum  $L$  and total electron-spin angular momentum  $S$  to be specified shortly. This subspace is spanned by

$$\begin{aligned} |\mathcal{S}\Psi_f^{(-)}\rangle &= \sum_{\alpha} |\psi_{\alpha}\rangle, \\ |\psi_{\alpha}\rangle &= \sum_{vl\lambda} \int dp p^2 \int dq q^2 \varphi_{vl}(p) \eta_{vl\lambda}(q) \\ &\quad \times |pq(l\lambda)LM_L\rangle_{\alpha} |(s\frac{1}{2})SM_S\rangle_{\alpha} \end{aligned} \quad (6)$$

using the usual Jacobi coordinates and angular momentum basis in momentum space.<sup>13</sup> In addition,  $\varphi_{vl}(p)$  is the known singlet ( $s=0$ ) bound state of pair  $\alpha$  having the quantum numbers  $(v, l)$  and  $\eta_{vl\lambda}(q)$  are unknown functions used in the variational principle (5) which describe the relative motion of atom  $\alpha$  compared to the center of mass of the bound pair. We recall<sup>9</sup> that in the zero-temperature limit the final state  $|\mathcal{S}\Psi_f^{(-)}\rangle$  has the quantum numbers  $L=2$  and  $S=\frac{1}{2}$ , while  $M_L=-1$  ( $-2$ ) and  $M_S=-\frac{1}{2}$  ( $\frac{1}{2}$ ) in the case of a single (double) spin-flip process. Furthermore, parity conservation requires  $l+\lambda$  to be even. Because the total wave function is symmetric under permutations of the hydrogen atoms, only odd  $l$  values are allowed,  $\eta_{vl\lambda}$  does not depend on  $\alpha$ , and the vectors  $|\psi_{\alpha}\rangle$  are related to each other by a cyclic permutation. It is important to point out that if we added to the bound states  $\varphi_{vl}(p)$  the continuum of singlet scattering states  $\varphi_{El}(p)$  the complete Hilbert space would be spanned by Eq. (6) and the variational principle would give an exact solution of the three-body Schrödinger equation.

Performing the variation within the subspace defined earlier, we easily find the one-dimensional coupled integral equations for the functions  $\eta_{vl\lambda}(q)$ :

$$\begin{aligned} \eta_{vl\lambda}(q) &= [1 - (-1)^l] \delta_{vv_f} \delta_{ll_f} \delta_{\lambda\lambda_f} \frac{\delta(q - q_f)}{qq_f} \\ &\quad + \frac{1}{E^- - E_{vl} - 3q^2/4m_H} \\ &\quad \times \sum_{v'l'\lambda'} \int dq' q'^2 V_{vl\lambda, v'l'\lambda'}(q, q') \eta_{v'l'\lambda'}(q'), \end{aligned} \quad (7)$$

where we made use of the linearity of the equations to simplify the inhomogeneous term.<sup>10</sup> This term corresponds to the physical requirement that  $|\mathcal{S}\Psi_f^{(-)}\rangle$  contains asymptotically the plane waves

$$\mathcal{S}|\varphi_{v_f l_f m_f} \mathbf{q}_f \rangle_\alpha | (0 \frac{1}{2}) \frac{1}{2} M_S \rangle_\alpha$$

with the total energy

$$E = E_{v_f l_f} + 3q_f^2/4m_H.$$

Moreover,  $E_{vl}$  is the energy of the bound state  $(v, l)$ ,  $m_H$

the hydrogen mass, and the factor  $[1 - (-1)^{l_f}]$  is a consequence of the statement made previously: Only odd values of the  $H_2$  molecular angular momentum are allowed.

Introducing the operator  $P = P_{12}P_{23} + P_{13}P_{23}$ , i.e., the sum of the two cyclic permutation operators, we find for the "interaction" matrix of Eq. (7)

$$V_{vl\lambda, v'l'\lambda'}(q, q') = \int dp p^2 \varphi_{vl}(p) \int dp' p'^2 \varphi_{v'l'}(p') \langle pq(l\lambda)LM_L |_\alpha \langle (0 \frac{1}{2}) \frac{1}{2} M_S | \times [(1+P)V^\alpha - P(E - H_\alpha)] | p'q'(l'\lambda')LM_L \rangle_\alpha | (0 \frac{1}{2}) \frac{1}{2} M_S \rangle_\alpha. \quad (8)$$

To see more clearly that rearrangement is indeed included, we consider the  $V^\alpha$  and  $PV^\alpha$  terms. The former gives rise to (in)elastic scattering without rearrangement. With only this term we recover the model of Ref. 10. In the context of the above-mentioned variational method this result is obtained if we asymmetrically restrict the subspace in which we solve the Schrödinger equation to all open channels (below breakup) of one particular pair  $\alpha$ . In contrast, the term  $PV^\alpha$  is responsible for the rearrangement process, since effectively a different particle pair is bound at either side of  $V^\alpha$ . Finally, the contribution  $-P(E - H_\alpha)$  accounts for the nonorthogonality of the vectors  $|\psi_\alpha\rangle$ . Intuitively, it guarantees that the Born series of Eq. (7) contains all possible interactions between the particles only once.

Formally Eq. (7) is identical to a two-body Lippmann-Schwinger equation and can be solved in the usual way by the introduction of the half-shell  $T$  (transition) matrix:

$$T_{vl\lambda, v'l'\lambda'}(q, q', E) = \sum_{v''l''\lambda''} \int dq' q'^2 V_{vl\lambda, v''l''\lambda''}(q, q') \times \eta_{v''l''\lambda''}(q'). \quad (9)$$

To evaluate the "interaction" matrix numerically we rewrite  $(1+P)V^\alpha$  as  $V_\alpha P + PV_\alpha P$  and use the angular momentum representation of  $P$ .<sup>13</sup> In the case of  $PV_\alpha P$  this leads to a sum of triple integrals. Each of the triple integrals can be reduced to an integral over a product of two integrals if we use cubic splines<sup>15</sup> to interpolate on the momentum arguments of the  $V_\alpha$  matrix. This procedure reduces the computational effort considerably but, nevertheless, the evaluation of the matrix elements of  $PV_\alpha P$  is the most time-consuming part of our calculation.

### III. RESULTS AND DISCUSSION

#### A. Numerical results

We solved the model described in the preceding section using Gauss-Legendre quadrature points to discretize the integral equation. To find converged results for the recombination rate constant  $L_g^{\text{eff}}$  we had to include all rotational levels with  $v = 12, 13, 14$  and in addition the  $(v, l)$  states  $(6-11, 1)$ ,  $(8-11, 3)$ , and  $(11, 5)$ . This leads to a total of 57 channels and a complex matrix equation for the

half-shell  $T$  matrix with a dimension of 1450. The inversion of this equation is performed by an  $LU$  decomposition of the kernel. As mentioned earlier, the main problem of the calculation is associated with the term  $PV_\alpha P$  in the "interaction" matrix. Using the set of channels given, we had to sum over all angular momenta up to  $l = 9$  in the calculation of this term. Fortunately, it turns out that only  $(13, 5)$ ,  $(13, 7)$ ,  $(14, 1)$ , and most importantly  $(14, 3)$  contribute significantly as final outgoing states to  $L_g^{\text{eff}}$ .

Before we present the results for the rate constant, we note that it is possible to extract immediately information on the collisional rovibrational relaxation of  $H_2$  in the  $1\Sigma_g^+$  electronic state, since we also evaluate the on-shell  $T$  matrix. In Fig. 1 we summarize the branching ratios for the dominant elastic and inelastic relaxation processes

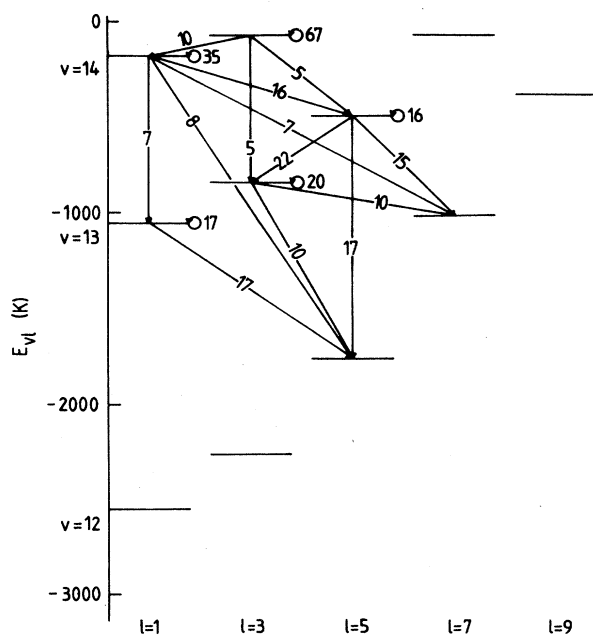


FIG. 1. The branching ratios (in %) for collisional rovibrational relaxation of highly excited  $H_2$  molecules. Also indicated is the percentage for elastic collisions.

from the (14,3) state downwards to the  $v=12$  and 13 rotational levels in an  $L=2$  collision. The probabilities depend, of course, on the relative momentum of atom and molecule and we have taken a value in agreement with the experimental situation at  $B \approx 10$  T, in which case the hydrogen molecules in the (14,3) state are formed in a recombination event with a kinetic energy of the order of 25 K. From these results we conclude that on average the (14,3) molecule loses an energy of about 170 K in the first collision with a  $b$  atom in the gas. Note that in our calculation only a total orbital angular momentum  $L=2$  is used. In a more complete treatment of the collisional relaxation angular momenta  $L=3$  and 4 would also have to be included. In view of this we do not give absolute cross sections but only branching ratios, which should at least give an impression of orders of magnitude.

We now turn to the determination of  $L_g^{\text{eff}}$ . In Fig. 2 we give the three-body recombination rate constant as a function of applied magnetic field and compare both with experiment<sup>3,6</sup> and our model without rearrangement.<sup>7</sup> Neglecting for a moment the resonance structure, which we discuss more thoroughly in Sec. III B, we notice in

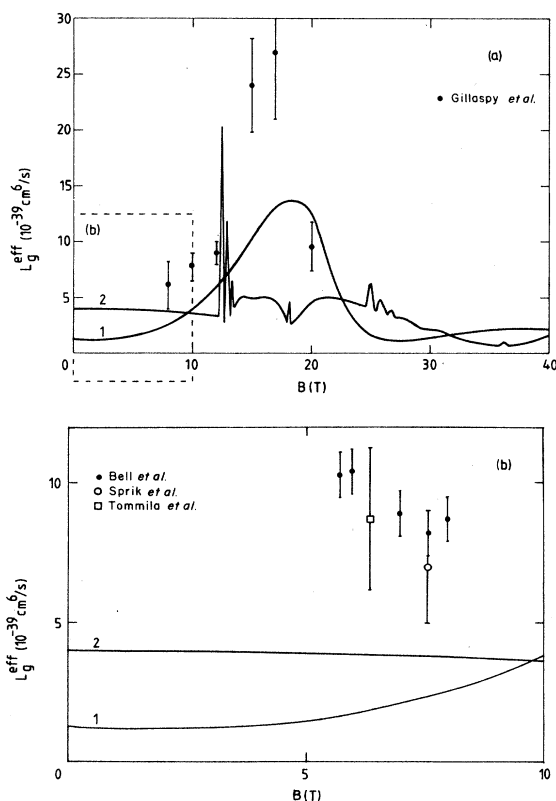


FIG. 2. The effective rate constant for three-body dipolar recombination of spin-polarized atomic hydrogen as a function of magnetic field. Part (a) shows the range 0–40 T, while part (b) gives  $L_g^{\text{eff}}$  below 10 T, in which range most of the experiments have been carried out. 1: The results of Refs. 10 and 7, without rearrangement. 2: The results of the present calculation including rearrangement. The experimental data is obtained from Refs. 3 and 6.

general an almost magnetic-field-independent behavior of the background. Physically this can be understood as follows: Kagan's model<sup>8</sup> predicted a steep increase of  $L_g^{\text{eff}}$  as a function of magnetic field, with a strong maximum around 15 T. This behavior can be explained on the basis of the overlap in momentum space. The initial state contains three almost immobile atoms and in the final state the atom-molecule interaction is omitted. Since the magnetic dipole interaction induces only small momentum transfers, there is a strong preference for a slow final outgoing atom. On the other hand, phase-space arguments associated with the small  $q_f$  values explain the decrease of  $L_g^{\text{eff}}$  beyond 15 T. Introducing an atom-molecule interaction in the rather weak form  $\frac{3}{4}V^{(0)} + \frac{1}{4}V^{(1)}$ , as we did in Refs. 7 and 10, shows already a tendency towards flattening. Although the repulsive  $V^{(1)}$  and the attractive  $V^{(0)}$  largely compensate one another in the relevant range of interatomic distances, the final state already contains such a range of momenta for any asymptotic  $q_f$  that the preference for smaller  $q_f$  is reduced. Much higher momenta are coupled in when the full singlet or triplet interaction  $V^{(s)}$  (depending on the parity of the relative angular momentum) is operating. We believe that this is the essential reason for the experimental behavior below 10 T, most clearly displayed by the MIT data, which even show a slight decrease. It follows from the preceding arguments that any future extension of the approach of the present paper, including the full strength of  $V^{(s)}$ , will lead to the same qualitative feature of the  $L_g^{\text{eff}}$  curve.

For fields in the range 10–20 T, we find a resonance-like behavior with maximum values far above the background. As we will describe in Sec. III B the explanation for this behavior is very different from the overlap arguments explaining Kagan's maximum. Although Kagan's model is in better agreement with the high-field data than our resonating-group approach [see Fig. 2(a) of Ref. 6], we stress that in our opinion it does not contain an essential ingredient. On the basis of the analysis of Sec. III B we believe that the recently measured high  $L_g^{\text{eff}}$  values can instead be explained by a bound-state calculation of the  $\text{H}_3$  molecule, which is, however, outside the scope of the present paper.

Quantitatively, there is still strong disagreement. Below 10 T our  $L_g^{\text{eff}}$  is a factor of 2 too small. In addition, the resonance peak at higher fields is too narrow and also does not have the correct position. As we will show shortly, this is due to an inadequate treatment of the resonances. To describe them correctly one needs to add singlet scattering states to the subspace defined by Eq. (6). However, due to divergences in the expressions for the "interaction" matrix, it is not possible to do so directly. One possibility is to include some bounded wave packets into the variational principle. Since a wave packet is not an eigenstate of the channel Hamiltonian, this results in a much more complicated equation which does not have the structure of a two-body Lippman-Schwinger equation. In any case it is useful to have more information on the wave function of the resonance states. This will enhance physical insight into the reaction mechanism and may ultimately lead to an adequate description of the recombination process.

### B. H<sub>3</sub> resonances

A convenient way to treat resonant scattering is by means of the Feshbach formalism.<sup>16</sup> To do so we divide the total Hilbert space into two subspaces, conventionally denoted by  $P$  and  $Q$ , containing the open and closed channels of the scattering problem, respectively. Bound states in  $Q$  space then correspond to resonances with finite lifetimes, because of the coupling between the two spaces.

In our case these subspaces can be characterized by the adiabatic states of three hydrogen atoms in a  $1s^3 E'$  electronic configuration, having a total electron spin  $S$  equal to  $\frac{1}{2}$ . The potential surfaces are found by diagonalizing the  $2 \times 2$  matrix

$$V_{ss'}(\{r_\alpha\}) = {}_\alpha \langle (s\frac{1}{2})SM_S | V | (s'\frac{1}{2})SM_S \rangle_\alpha,$$

which depends parametrically on the distances  $\{r_\alpha\}$  between the particles. Introducing the notation

$$V(r_\alpha) = [V^{(1)}(r_\alpha) + V^{(0)}(r_\alpha)]/2$$

and

$$\Delta(r_\alpha) = V^{(1)}(r_\alpha) - V^{(0)}(r_\alpha)$$

we easily find for the eigenvalues

$$V_{Q,P}(\{r_\alpha\}) = \sum_\alpha V(r_\alpha) \pm \frac{1}{2} \left[ \sum_\alpha \Delta^2(r_\alpha) - \sum_{\alpha < \alpha'} \Delta(r_\alpha)\Delta(r_{\alpha'}) \right]^{1/2}, \quad (10)$$

with  $Q(P)$  corresponding to the  $+(-)$  sign. If atom  $\alpha'$  is far away from the other two atoms, these energy surfaces reduce to the singlet and triplet potentials:

$$V_{Q,P}(\{r_\alpha\}) = V(r_{\alpha'}) \pm \frac{1}{2}\Delta(r_{\alpha'}) = V^{(1,0)}(r_{\alpha'}),$$

leading to the conclusion that below breakup the open and closed channels of the atom-molecule collision can indeed be associated with the adiabatic states of the three-atom system.

We now concentrate on  $Q$  space. For fixed  $\sum_\alpha V(r_\alpha)$  the energy surface has a minimum if the atoms are in an equilateral configuration, because in that case the square root in Eq. (10) is zero. Therefore, one would like to introduce coordinates to describe the vibrations around this configuration. Since the depth of the  $Q$  potential surface is about 17 000 K and the calculations of the preceding section show resonances with binding energies in the range of 35–50 K, we are especially interested in highly excited states near the continuum ("long-range H<sub>3</sub> $\infty$  molecules"<sup>17</sup>). In this case the usual normal coordinates are not adequate. However, it is possible to introduce the (external) symmetry coordinates<sup>18</sup> of an equilateral triangle having symmetry  $D_{3h}$ , which we denote by  $S_i$  ( $i=1,2,3$ ).<sup>19</sup> In Fig. 3 we see that  $S_0$  corresponds to the symmetric-stretching mode, whereas  $S_1$  and  $S_2$  are two possible bending modes of the H<sub>3</sub> molecule.

The square root in Eq. (10) reducing to zero in the equilateral configuration, small deviations from this

configuration, described by  $S_1$  and  $S_2$ , cause a steep linear<sup>19</sup> increase in the potential energy. Physically, this means that the H<sub>3</sub> molecule carries out small-amplitude, rapid vibrations around an equilateral configuration that is vibrating more slowly with a large  $S_0$  amplitude. In the following we, therefore, consider only potential terms up to first order in  $S_1$  and  $S_2$  but take all orders of  $S_0$  into account.

The Hamiltonian of the rotating and vibrating nonlinear molecule is given by<sup>18,20</sup>

$$H = \frac{1}{2}(\mathbf{L}-\mathbf{j})\tilde{\mu}(\mathbf{L}-\mathbf{j}) - \frac{\hbar^2}{8}\text{Tr}(\tilde{\mu}) - \frac{\hbar^2}{2m_H} \sum_i \frac{\partial^2}{\partial S_i^2} + V_Q(\{S_i\}), \quad (11)$$

where  $\mathbf{L}-\mathbf{j}$  is the rotational angular momentum,  $\mathbf{j}$  the vi-

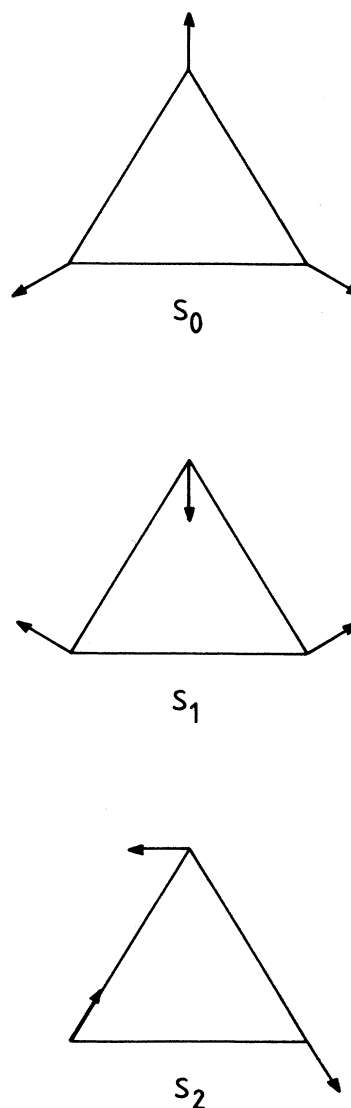


FIG. 3. The vibrational (external) symmetry coordinates  $S_i$  of an equilateral triangle.

brational angular momentum, and  $\vec{\mu}$  the reciprocal inertia tensor, all defined with respect to an Eckart frame<sup>21</sup> moving with the molecule. If we choose, in particular, the frame attached to the instantaneous orientation of the equilateral triangle we find that the vibrational angular momentum is perpendicular to the plane of the  $H_3$  molecule and equal to

$$j_z = \left[ S_2 \frac{\hbar}{i} \frac{\partial}{\partial S_1} - S_1 \frac{\hbar}{i} \frac{\partial}{\partial S_2} \right]. \quad (12)$$

Up to first order in  $S_1$  and  $S_2$  the tensor  $\vec{\mu}$  turns out to be

$$\vec{\mu} = \frac{2}{m_H S_0^3} \begin{pmatrix} S_0 + 2S_1 & 2S_2 & 0 \\ 2S_2 & S_0 - 2S_1 & 0 \\ 0 & 0 & \frac{1}{2}S_0 \end{pmatrix}. \quad (13)$$

Substituting these results into Eq. (11) and introducing polar coordinates  $(S_r, \vartheta)$  instead of  $(S_1, S_2)$  we find the Hamiltonian

$$H = H^{\text{rot}} + H^{\text{vib}} + H^{\text{cor}} + V, \quad (14)$$

with

$$H^{\text{rot}} + H^{\text{vib}} + V = \left[ -\frac{\hbar^2}{2m_H} \frac{\partial^2}{\partial S_0^2} + \frac{\hbar^2}{2m_H S_0^2} [2L(L+1) - K^2 + 2KN + N^2 - \frac{5}{4}] \right. \\ \left. + 3V(S_0) - \frac{\hbar^2}{2m_H} \frac{\partial^2}{\partial S_r^2} + \frac{\hbar^2}{2m_H S_r^2} (N^2 - \frac{1}{4}) + \beta(S_0) S_r \right] \quad (15)$$

and  $H^{\text{cor}}$  a small perturbation due to the Coriolis force, which couples the rotation and vibration of the molecule. Explicitly it reads

$$H^{\text{cor}} = \frac{S_r}{m_H S_0^3} (e^{i\vartheta} L_-^2 + e^{-i\vartheta} L_+^2). \quad (16)$$

In the foregoing expressions we have written the eigenvalues of  $L_z$  and  $j_z$  as  $\hbar K$  and  $-\hbar N$ , respectively. Furthermore, in agreement with the approximations made, we have also expanded  $V_Q(\{S_i\})$  up to first order in  $S_r$ , leading to

$$V_Q(\{S_i\}) = 3V(S_0) + \left| \frac{3}{4} \frac{d\Delta(S_0)}{dS_0} \right| S_r \\ \equiv 3V(S_0) + \beta(S_0) S_r,$$

which shows the above-mentioned linear dependence of the potential surface on  $S_r$ .

Neglecting the Coriolis coupling for a moment we see that both  $K$  and  $N$  are good quantum numbers, because of the  $D_{3h}$  symmetry of the Hamiltonian of Eq. (15). The splitting of a particular vibrational level of the stretching mode, due to both the bending modes and the rotation of the  $H_3$  molecule, is shown qualitatively in Fig. 4(a), where

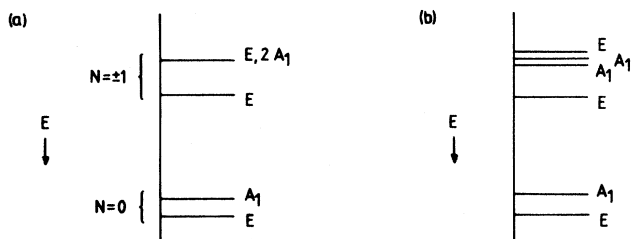


FIG. 4. The energy splitting of a vibrational level of the  $H_3$  stretching mode due to the bending modes and molecular rotation. (a) Without Coriolis coupling. (b) With Coriolis coupling.

the states with odd parity ( $K = \pm 1$ ) are not considered, since they do not participate in the recombination process (cf. Sec. II). Also indicated is the degeneracy and the ( $D_3$ ) symmetry class of the states.

Including  $H^{\text{cor}}$  breaks the  $D_{3h}$  symmetry down to  $D_3$  and removes the degeneracy of the energy levels as is shown in Fig. 4(b). Only the levels corresponding to an  $E$ -type symmetry still have twofold degeneracy, which can be characterized by the conserved quantum number  $2N - K$ . Most importantly, we note that the spectrum of the (perturbed)  $N = \pm 1$  states corresponds to the spectrum found in the calculation of Sec. III A, keeping in mind that the single and double spin-flip contributions to the rate constant cause the repetitive structure of  $L_g^{\text{eff}}(B)$  at twice the magnetic field strength. From the numerically observed splitting between the two  $E$ -type levels we can estimate the average distance  $\langle S_0 \rangle$  between the particles to be about  $7a_0$ . This gives the reason why the resonances are inadequately treated in our model: In the singlet bound states that span the subspace (6) the particles have on average a separation of at most  $5a_0$ , the (14,3) state having the largest dimensions. We thus have to include scattering states to make it possible for the particles to have larger separation. Extending the subspace in this manner we expect the resonances to be much broader, because the coupling with the  $P$  space is enhanced, leading to a shorter resonance lifetime.

#### IV. CONCLUSIONS

We have shown that in the three-body recombination process of spin-polarized atomic hydrogen, resonances play a crucial role and come into play when the possibility of rearrangement is included. In addition, we have identified these resonances with adiabatic states of an  $H_3$  molecule in an almost equilateral configuration. Nonadiabatic effects, due to the finite kinetic energy of the atoms, lead to decay and therefore to a finite resonance

lifetime. Our resonating-group method is able to explain the slow decrease of the recombination rate below 10 T, as well as the occurrence of a much higher recombination rate at stronger fields. Despite this qualitative agreement with experiment, some features require a more thorough analysis which is at present out of reach: Below 10 T our results are still a factor of 2 lower than experiment, while the resonance peaks at higher fields are too narrow and occur at too low a field value. This discrepancy requires a more adequate treatment of the  $H_3$  resonance states, which are expected to have much wider interatomic separation than even in the case of a (14,3)  $H_2$  molecule. Including singlet scattering states to allow for a large separation seems to be difficult in the context of the resonating-group theory, since it involves nonlocalized wave functions. One possibility would be to use wave packets instead.

Another approach, which has the advantage of using

eigenstates of the channel Hamiltonian, was successfully applied to the triton<sup>22</sup> and may also be used here. Since the three-body breakup channel is closed, the two-body continuum neglected in the ansatz (6) has to build up only a decaying state. Therefore, the channel Hamiltonian can be supplemented by an auxiliary confining potential conveniently chosen as a harmonic oscillator. This procedure leads to a discrete representation of the continuum and thus to a natural and rigorous extension of the calculations presented here.

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