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Nonadiabatic Coupling in Fine-Structure Transitions of Alkali Atoms Induced by Diatomic Molecules

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Fine-structure transitions of alkali atoms induced by collisions with diatomic molecules are shown to be strongly influenced by a dynamical feature that is completely absent when the collision partner is a rare gas. The effect is a nonadiabatic coupling caused by the anisotropy of the molecule. Calculations for $\mathrm{Rb}(5^2P_{1/2})+\mathrm{H}_2$ and for $\mathrm{Rb}(5^2P_{1/2})+\mathrm{He}$ are in good agreement with recent experiments and explain the dramatic difference between these two systems.

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The collisional mixing of fine-structure levels of alkali atoms by various perturbers illustrates the interplay of several fundamental mechanisms. The process is

$$A(^2P_{1/2})+X\to A(^2P_{3/2})+X\,, \tag{1}$$

where A is an alkali and X may be a rare gas or a diatomic molecule. In the former case, the scattering has been extensively investigated, and is well understood in terms of the analysis of Nikitin.[1] When the target is a molecule, experimental studies have generally shown that the cross section for process (1) becomes larger, sometimes by more than an order of magnitude. Previous theoretical analysis has generally invoked two mechanisms to explain such differences. First, passage through an intermediate complex A^+X^- is sometimes assumed to cause mixing of the fine-structure levels.[2] Second, if there is a near resonance between the fine-structure splitting $\Delta\epsilon$ and a rotational transition of the molecule, the cross section may be enhanced.[3-6] In the present paper we present another mechanism, which has not previously been identified, and whose origin is essentially the simplest distinguishing feature of the alkali-molecule system, its reduced symmetry.

For collisions between an alkali atom and a rare gas, Nikitin[1] has shown how the electronic states of H_{el} and the fine-structure splitting $\Delta\epsilon$ determine the adiabatic states and couplings of the full Hamiltonian $H=H_{\mathrm{el}}+H_{\mathrm{so}}$ (electronic plus spin orbit). The Σ and Π states of H_{el} are degenerate asymptotically, and split as the internuclear distance R decreases. Corresponding adiabatic states $A\,^2\Pi_{1/2}$ and $B\,^2\Sigma_{1/2}$ of H are asymptotically separated by the fine-structure splitting $\Delta\epsilon$. They are strongly coupled near the region where the splitting of the states Σ and Π of H_{el} is equal to $\Delta\epsilon$. For rare-gas targets, there are of course two Π electronic states, which are degenerate. For molecular targets, the nomenclature changes somewhat, but effectively the degeneracy of the two Π states is lifted by the anisotropy of the molecule. Consequently the adiabatic states of $H_{\mathrm{el}}+H_{\mathrm{so}}$ experience an additional coupling near the region where the splitting of the two Π-like states of H_{el} is equal to $\Delta\epsilon$.

I will illustrate this effect by the following analysis of the collision. Let the system alkali plus diatomic molecule be described by an electronic Hamiltonian H_{el} whose matrix elements in the basis of the alkali orbitals np_x, np_y, and np_z are H_{xx}, H_{xy}, etc. This Hamiltonian has been discussed by Rebentrost and Lester.[4] The matrix elements of H_{el} are functions of R and θ, which define in the usual way the distance from the alkali to the molecule, and the orientation of the molecule. We now expand the components of H_{el} in Legendre polynomials and consider only the P_0 part. The only nonzero terms are denoted by $H_{xx}{}^0(R)$, $H_{yy}{}^0(R)$, and $H_{zz}{}^0(R)$. It is crucial to note that even the isotropic component of $H_{xx}-H_{yy}$ is nonzero. This splitting may be modeled by use of the value obtained from the asymptotic quadrupole-quadrupole interaction,[4a] which is $-(3C/2)R^{-5}\sin^2\theta$, where C is the product of the qudrupole moments of the alkali and of the diatomic molecule. Then

$$H_{xx}{}^0-H_{yy}{}^0=-CR^{-5}\,. \tag{2}$$

Generally speaking, we expect that $H_{zz}{}^0$, which corresponds to the Σ state of a collinear system, will become repulsive because of electron overlap faster than the $H_{xx}{}^0$ and $H_{yy}{}^0$ curves will split. We may thus expect that for part of the collision, $H_{zz}{}^0$ and $\frac{1}{2}(H_{xx}{}^0+H_{yy}{}^0)$ will act essentially as the

Σ and Π states of a collinear system. New features will appear when R becomes sufficiently small that $H_{xx}{}^0 - H_{yy}{}^0 \approx \Delta\epsilon$.

We now consider the eigenstates of $H_{\text{el}} + H_{\text{so}}$. When spin is included it is convenient to rewrite the matrix elements in terms of the new basis functions $|npjm_j\rangle$. Neglecting rotational coupling, the Hamiltonian splits into two 3×3 blocks, which for the purposes of this model are completely equivalent. The basis states for one of these blocks are $|np\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle$, $|np\,\tfrac{3}{2}\,\tfrac{1}{2}\rangle$, and $|np\,\tfrac{3}{2}\,-\tfrac{3}{2}\rangle$. Defining

$$\alpha = [H_{zz}{}^0 - \tfrac{1}{2}(H_{xx}{}^0 + H_{yy}{}^0)]/\Delta\epsilon, \tag{3}$$

$$\beta = (H_{xx}{}^0 - H_{yy}{}^0)/\Delta\epsilon, \tag{4}$$

$$\overline{V} = \tfrac{1}{3}(H_{xx}{}^0 + H_{yy}{}^0 + H_{zz}{}^0), \tag{5}$$

we obtain the matrix elements of $H_{\text{el}} + H_{\text{so}}$:

$$H = \overline{V}\,\underline{1} + \Delta\epsilon \left| \begin{array}{lll} 0 & \tfrac{1}{3}\times 2^{1/2}\alpha & -\tfrac{1}{6}\times 6^{1/2}\beta \\ \tfrac{1}{3}\times 2^{1/2}\alpha & \tfrac{1}{3}\alpha + 1 & \tfrac{1}{6}\times 3^{1/2}\beta \\ -\tfrac{1}{6}\times 6^{1/2}\beta & \tfrac{1}{6}\times 3^{1/2}\beta & (-\tfrac{1}{3}\alpha) + 1 \end{array} \right| . \tag{6}$$

If this Hamiltonian is diagonalized at each R, we obtain the adiabatic potential curves. Given the general behavior of H_{el} discussed above, these potentials will have the form shown in Fig. 1. The regions I, II, and III in the figure are separated by the points R_1 and R_2, where $\alpha(R_1) = 1$ and $\beta(R_2) = 1$. In regions I and II the splitting $H_{xx}{}^0 - H_{yy}{}^0$ is generally small compared to $\Delta\epsilon$ and is ignored. Then the situation corresponds to the alkali–rare-gas case analyzed by Nikitin.[1] In this limit ($\beta = 0$), the eigenstates of H are, in order of increasing energy,

$$\psi_1 = \cos\varphi_1 |np\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle - \sin\varphi_1 |np\,\tfrac{3}{2}\,\tfrac{1}{2}\rangle, \tag{7}$$

$$\psi_2 = |np\,\tfrac{3}{2}\,-\tfrac{3}{2}\rangle, \tag{8}$$

$$\psi_3 = \sin\varphi_1 |np\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle + \cos\varphi_1 |np\,\tfrac{3}{2}\,\tfrac{1}{2}\rangle, \tag{9}$$

where

$$\tan 2\varphi_1 = 2^{3/2}\alpha/(\alpha + 3). \tag{10}$$

It is the R dependence of the wave functions ψ_1 and ψ_3, through Eqs. (3) and (10), that causes a nonadiabatic coupling between these states.

The transition from region II to region III occurs when $\beta \approx 1$. If $\alpha \gg 1$ near R_2, the eigenstate ψ_3 retains the form corresponding to the limiting value $\tan 2\varphi_1 = 2^{3/2}$. However, the wave functions ψ_1 and ψ_2 depend strongly on R through β as follows:

$$\psi_1 = \cos\varphi_2 [(\tfrac{2}{3})^{1/2} |np\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle - (\tfrac{1}{3})^{1/2} |np\,\tfrac{3}{2}\,\tfrac{1}{2}\rangle] - \sin\varphi_2 |np\,\tfrac{3}{2}\,-\tfrac{3}{2}\rangle, \tag{11}$$

$$\psi_2 = \sin\varphi_2 [(\tfrac{2}{3})^{1/2} |np\,\tfrac{1}{2}\,\tfrac{1}{2}\rangle - (\tfrac{1}{3})^{1/2} |np\,\tfrac{3}{2}\,\tfrac{1}{2}\rangle] + \cos\varphi_2 |np\,\tfrac{3}{2}\,-\tfrac{3}{2}\rangle, \tag{12}$$

where

$$\tan 2\varphi_2 = 3\beta/2. \tag{13}$$

This R dependence of the wave function near R_2 gives a second region of nonadiabatic coupling.

I now consider a model in which the couplings at R_1 and R_2 are treated as two independent curve crossings. Then p_1 gives the probability for a transition between ψ_1 and ψ_3 at R_1, and p_2 gives the probability for a transition between ψ_1 and ψ_2 at R_2. We calculate p_1 and p_2 by applying recently developed formulas[7] based on the Magnus approximation. The result is

$$p_i = \sin^2 \left| \int_0^\infty \dot{\varphi}_i(t) \exp\left[i \int_0^t \Delta\lambda_i(t')\,dt'\right] dt \right|, \tag{14}$$

where $\dot{\varphi}_i$ is the time derivative, and we assume a rectilinear trajectory $R(t) = (b^2 + v^2 t^2)^{1/2}$. $\Delta\lambda_i$ is the difference of the adiabatic eigenvalues of the two states that are coupled:

$$\Delta\lambda_1 = \Delta\epsilon(\alpha^2 + \tfrac{2}{3}\alpha + 1)^{1/2}, \tag{15}$$

$$\Delta\lambda_2 = \Delta\epsilon(\beta^2 + \tfrac{4}{9})^{1/2}. \tag{16}$$

By following the various sequences of crossings that can lead from the initial state ψ_1 ($j = \tfrac{1}{2}$) to a final state ψ_2 or ψ_3 ($j = \tfrac{3}{2}$), we obtain the probability for changing fine-structure level:

$$P = 2p_1(1 - p_1) + 2p_2(1 - p_2)(1 - p_1)^2. \tag{17}$$

The cross section is obtained by integrating P over the impact parameter b for each velocity v.

I have performed calculations using this two-crossing model for the system $\text{Rb}(5^2P_{1/2}) + \text{H}_2$, and also for $\text{Rb}(5^2P_{1/2}) + \text{He}$. Since we expect the interaction of an alkali with H_2 to be similar to the interaction with He, I used the same potentials for $H_{zz}{}^0$ and $\tfrac{1}{2}(H_{xx}{}^0 + H_{yy}{}^0)$ for both systems. The Σ and Π potential curves for $\text{Rb}(5^2P) + \text{He}$ calculated by Baylis[8] were used. For H_2, Eq. (2) was used for all values of R with the value $C = 21.44$ a.u. determined from accurate values of the two quadrupole moments.[4a,8b] The comparison between these two calculations highlights the role of the second crossing, since the value

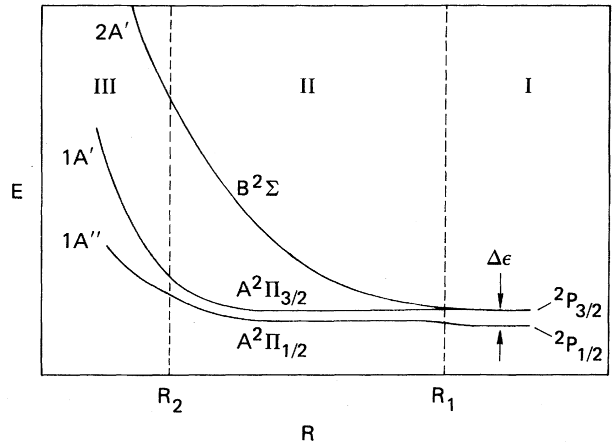

FIG. 1. Schematic diagram of the adiabatic potentials of $H = H_{el} + H_{so}$ for an alkali atom plus a diatomic molecule. In regions I and II the system is analogous to an alkali plus a rare gas. For the rare gas, there exist two degenerate Π states of H_{el}, and the separation of the corresponding states of H is uniformly $\frac{2}{3}\Delta\epsilon$ for $R \lesssim R_1$. For the diatomic partner, the Π-like states of H_{el} are split significantly for $R \lesssim R_2$, so the corresponding states of H diverge and approach the $1A''$ and $1A'$ states of H_{el}.

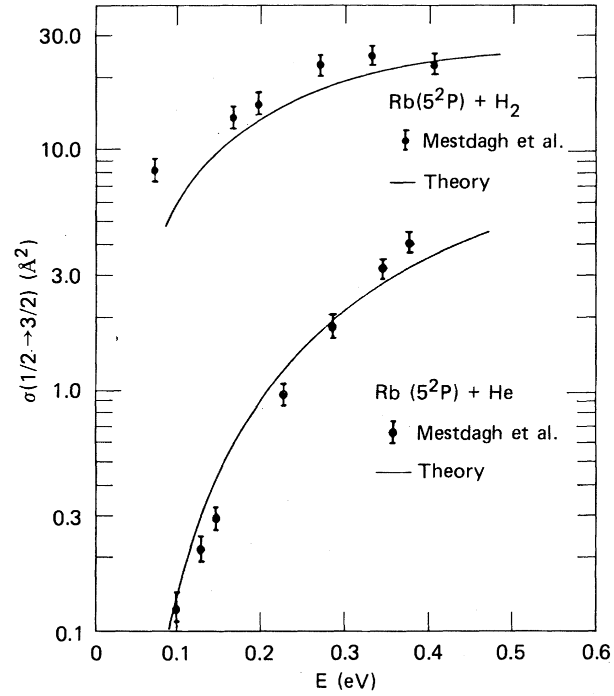

FIG. 2. Comparison of the calculations based on two independent curve crossings with the data of Mestdagh *et al*. (Ref. 10).

of p_1 is the same in each case, but $p_2 \equiv 0$ for Rb + He. For the He case, the present calculations are in good agreement with coupled-channels calculations of Olson,[9] who used the same potentials. The results for Rb($5^2P_{1/2}$) + H$_2$ show a dramatic effect due to the second crossing. The comparison with recent experiments[10] shown in Fig. 2 indicates that the effect can account for a difference of nearly 2 orders of magnitude in the cross sections at 0.1 eV.

Of course, the other mechanisms previously mentioned might also affect the scattering. For example, Andreev and Voronin[2] have discussed how fine-structure transitions in Cs($6^2P_{3/2}$) + N$_2$ may proceed by an intermediate ionic complex $Cs^+ + N_2^-$. Such an intermediate complex $Rb^+ + H_2^-$ is also possible. However, the radius R_c at which such ionic configurations contribute to the wave function is smaller for systems involving H$_2$ than for those involving N$_2$. I estimate $R_c \approx 5a_0$ for Rb-H$_2$; I have found that p_2 is significant for impact parameters larger than this value. In addition, with an ionic complex model it is necessary to account for a large quenching cross section ($^2P \to {}^2S$ transitions) so that only a fraction of trajectories "survive" in the ^2P level. Another mechanism that clearly plays a role in certain systems is simultaneous excitation of the fine-structure transition and rotational deexcitation of the molecule.[3-6] If these two transitions are nearly in resonance, one expects a greatly enhanced cross section. This mechanism invokes higher-order terms in the interaction potential to drive the rotational transitions. The present mechanism, although caused essentially by the asymmetry of the molecule, persists in the lowest order (P_0) and is therefore independent of the rotational motion.

The purpose of this Letter has been to present a new mechanism that comes into play when fine-structure transitions are induced by molecules rather than atoms. A model has been developed and used to compare the systems Rb(5^2P)-H$_2$ and Rb(5^2P)-He. The results clearly indicate that the additional region of nonadiabatic coupling (or curve crossing) induced by the anisotropy of the molecule can lead to significant enhancement of the transition probability.

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Quantum-Mechanical State-to-State Differential Cross Sections for the Reaction $F + H_2 \rightarrow H + HF$

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This communication presents the first nonperturbative quantum-mechanical calculation for state-resolved angular differential cross sections for a chemical rearrangement for which experimental results are available. The reaction studied, $F + H_2 \rightarrow H + HF$, is an important prototype for understanding reaction dynamics and is one of the few for which comparisons of experiment and theory are possible. The significant features of the state-to-state angular distributions for this reaction observed experimentally are reproduced by this study.

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In this communication we report quantum-mechanical calculations of state-resolved angular differential cross sections for the reaction[1]

$$F + H_2(v_i = 0, j_i = 0) \rightarrow HF(v_f = 0, 1, 2, 3) + H. \quad (1)$$

The final products are resolved so far as the final vibrational state of the HF is concerned but are degeneracy averaged and summed over final rotational states. This system is of great importance because Sparks *et al.*[2] have recently reported the first experimental determination of such state-resolved angular distributions for a reactive molecular collision. The system is of further importance for its role in the (F_2, H_2) laser system and the fact that it represents one of the main prototype reactions for studying energy disposal in reactive collisions. The calculations were performed by using the so-called Muckerman-V potential surface,[3] and as will be seen, they yield results which agree with the experiments of Sparks *et al.*[2] These results represent the first successful computation of such phase-sensitive cross sections which can be compared with experiment.

The physical content of the approximation we employ is based on the recognition that some nuclear motion degrees of freedom in molecular collisions are slower than others. As a conse-