

Spin-change cross-sections for collisions between alkali atoms

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A simple procedure is described for the calculation of the interactions between two atoms at intermediate separations and the spin-change cross-sections for collisions between pairs of atoms selected from hydrogen, lithium, sodium, potassium, rubidium and caesium are calculated. Satisfactory agreement with the measured values is obtained.

1. INTRODUCTION

A variety of techniques has been used to observe the effects of spin-change collisions on the populations of the ground state hyperfine multiplets of alkali metal vapours and values of the spin-change cross-section have been determined for the mixtures Rb-Cs (Dehmelt 1958), Na-K (Franken, Sands & Hobart 1958), Na-Rb (Novick & Peters 1958), Na-Na (Anderson & Ramsey 1963), Rb-Rb (Bouchiart & Brossel 1962; Jarrett 1964; Moos & Sands 1964) and Cs-Cs (Moos & Sands 1964).

The quantal description is formally analogous to that for resonance charge transfer (Dalgarno 1961) and in order to compute the spin-change cross-section it is necessary to determine the difference between the interaction potentials of the two possible symmetry states formed by the atom.

2. THEORY

We consider a collision of two atoms A and B in 2S states with spatial eigenfunctions $\psi_A(\mathbf{r}_A, r_1)$ and $\psi_B(\mathbf{r}_B, r_2)$ respectively, where \mathbf{r}_A and \mathbf{r}_B denote collectively the position vectors of the core electrons and \mathbf{r}_1 and \mathbf{r}_2 denote the position vectors of the valence electrons. We consider in particular a collision in which atom A undergoes spin change such that the total spin of A compounded of the spin of electron 1 and the spin of nucleus A is altered and we assume that the process is an elastic one. Let \mathbf{R} be the vector joining the centres of mass of atoms A and B , let $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ be the spin coordinate of nucleus A . Then if we couple the spins of electrons 1 and 2 to form a resultant S with projection M_S , described by a spin wavefunction $\chi(S, M_S)$, the wavefunction of the collision system has the asymptotic form

$$\Psi(\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_1, \mathbf{r}_2; \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_A) \underset{R \rightarrow \infty}{\sim} \psi_A(\mathbf{r}_A, r_1) \psi_B(\mathbf{r}_B, r_2) [\chi(S_1 M_S) \delta(\mu_A | \boldsymbol{\sigma}_A) \exp(i\mathbf{k} \cdot \mathbf{R}) \\ + \sum_{S'} \sum_{M_{S'}} \sum_{\mu_{A'}} \chi(S', M_{S'}) \delta(\mu_{A'} | \boldsymbol{\sigma}_A) f(S, M_S, \mu_A; S', M_{S'}, \mu_{A'}; \hat{\mathbf{R}}) R^{-1} \exp(ikR)],$$

where \mathbf{k} is the relative momentum and we may omit the spin function of nucleus B . With this coupling scheme, the scattering amplitude may be written

$$f(S, M_S, \mu_A; S', M_{S'}, \mu_{A'}; \hat{\mathbf{R}}) = f(S; \hat{\mathbf{R}})$$

provided spin-orbit and spin-spin interactions may be neglected.

We now employ a representation in which the spin of electron 1 is coupled to the spin I of nucleus A to form a resultant total spin F with projection M_F . Then asymptotically the wave function may be written

$$\Psi(\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_1, \mathbf{r}_2; \sigma_1, \sigma_2, \sigma_A) \underset{R \rightarrow \infty}{\sim} \psi_A(\mathbf{r}_A, r_1) \psi_B(\mathbf{r}_B, r_2) \chi(F, M_F) \delta(\mu_2 | \sigma_2) \exp(i\mathbf{k} \cdot \mathbf{R}) + \sum_{F'} \sum_{M_{F'}} \sum_{\mu'_2} \chi(F', M_{F'}) \delta(\mu'_2 | \sigma_2) f(F, M_F, \mu_2; F', M_{F'}, \mu'_2; \hat{\mathbf{R}}) R^{-1} \exp(ikR).$$

A straightforward recoupling yields the result that

$$f(F, M_F, \mu_2; F', M_{F'}, \mu'_2; \hat{\mathbf{R}}) = \sum_S \sum_{F_T} \sum_{M_T} (FM_F \frac{1}{2} \mu_2 | F_T M_T) \times (F' M_{F'} \frac{1}{2} \mu'_2 | F_T M_T) (2S + 1) (2F + 1)^{\frac{1}{2}} (2F' + 1)^{\frac{1}{2}} \times W(\frac{1}{2}, \frac{1}{2}, I, F_T; S, F) W(\frac{1}{2}, \frac{1}{2}, I, F_T; S, F') f(S; \hat{\mathbf{R}}),$$

where the first two factors are Clebsch–Gordon coefficients and the W 's are Racah coefficients.

The differential cross-section is given by

$$q(F, F'; \hat{\mathbf{R}}) = \frac{1}{2(2F + 1)} \sum_{M_F} \sum_{\mu_2} \sum_{M_{F'}} \sum_{\mu'_2} |f(F, M_F, \mu_2; F', M_{F'}, \mu'_2; \hat{\mathbf{R}})|^2 = \frac{1}{2(2F + 1)} \sum_{F_T} \sum_{M_T} | \sum_S \phi(S) f(S) |^2$$

where
$$\phi(S) = (2S + 1) (2F + 1)^{\frac{1}{2}} (2F' + 1)^{\frac{1}{2}} \times W(\frac{1}{2}, \frac{1}{2}, I, F_T; S, F) W(\frac{1}{2}, \frac{1}{2}, I, F_T; S, F').$$

Then writing

$$\sum_S f(S) \phi(S) = f(1) \{ \phi(0) + \phi(1) \} + \phi(0) \{ f(0) - f(1) \}$$

and using the relationships

$$\sum_e (2e + 1) (2f + 1) W(a, b, c, d; e, f) W(a, b, c, d; e, g) = \delta_{fg}$$

and

$$W(a, b, c, d; 0, f) = \frac{(-1)^{f-b-d} \delta_{ab} \delta_{cd}}{[(2b + 1)(2a + 1)]^{\frac{1}{2}}}$$

it follows that

$$\sum_S f(S) \phi(S) = f(1) \delta_{FF'} - \{ f(0) - f(1) \} [(2F + 1)(2F' + 1)]^{\frac{1}{2}} \frac{(-)^{F+F'} \delta_{IF_T}}{2(2I + 1)}.$$

Hence if $F' \neq F$,

$$q(F, F'; \hat{\mathbf{R}}) = \frac{(2F' + 1)}{8(2I + 1)} |f(0) - f(1)|^2.$$

The scattering amplitudes $f(0)$ and $f(1)$ may be expressed in terms of the phase shifts $\eta_l(0)$ and $\eta_l(1)$ for elastic scattering by the interaction potentials $V(0)$ and $V(1)$ in respectively the singlet and triplet states as

$$f(S) = \frac{1}{2ik} \sum_{l=0}^{\infty} \{ \exp(2i\eta_l(S)) - 1 \} (2l + 1) P_l(\cos \theta)$$

and the total spin-change cross-section becomes

$$Q(F, F') = \frac{\pi(2F' + 1)}{2k^2(2I + 1)} \sum_{l=0}^{\infty} (2l + 1) \sin^2 \{ \eta_l(0) - \eta_l(1) \}$$

in agreement with Dalgarno (1961) for the special case $I = \frac{1}{2}$.

It is useful to introduce a spin-exchange cross-section

$$Q_{\text{ex.}} = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \{ \eta_l(0) - \eta_l(1) \}$$

which is independent of I and F' . Then

$$Q(F, F') = \frac{2F' + 1}{2(2I + 1)} Q_{\text{ex.}}$$

In the summations over l there will usually be significant contributions from large values of l and we may proceed to a semi-classical approximation given by Massey & Mohr (1934) according to which

$$Q_{\text{ex.}} = 2\pi \int_0^{\infty} p \sin^2 \{ \zeta(p) \} dp,$$

where

$$\zeta(p) = \frac{1}{v} \int_p^{\infty} \frac{R \{ V(0|R) - V(1|R) \}}{(R^2 - p^2)^{\frac{1}{2}}} dR,$$

v being the relative velocity of the colliding atoms. More elaborate calculations by Smith (1963) and by Dalgarno & Henry (1964) show that the approximation is satisfactory for the collision of a pair of hydrogen atoms.

Firsov (1951) has suggested the further approximation

$$Q_{\text{ex.}} = 2\pi \int_0^{\infty} p \sin^2 \{ \zeta(p) \} dp = \frac{1}{2} \pi p^{*2},$$

where

$$|\zeta(p^*)| = 1/\pi,$$

and Bates & Boyd (1962) have demonstrated its accuracy for potentials varying as R^{-n} .

3. THE INTERACTION POTENTIALS

Firsov (1951) has given a simple expression for $V(0) - V(1)$ for an ion and its parent atom (cf. Bates & McCarroll 1962) but its extension to a pair of atoms is not obvious. We have used an alternative procedure which is equally applicable to ion-atom and atom-atom interactions.

If H is the complete Hamiltonian of the system with the nuclei A and B held fixed at a distance R apart, the singlet and triplet wavefunctions $\chi_0(\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_1, \mathbf{r}_2; R)$ and $\chi_1(\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_1, \mathbf{r}_2; R)$ satisfy the equations

$$\{H - V(0|R)\} \chi_0 = 0,$$

$$\{H - V(1|R)\} \chi_1 = 0.$$

Ignoring exchange with the core electrons, we may write

$$\chi_0 = f_{AB}(\mathbf{r}_A, \mathbf{r}_B) \{ \phi(r_{1A}) \psi(r_{2B}) + \phi(r_{2A}) \psi(r_{1B}) \},$$

$$\chi_1 = f_{AB}(\mathbf{r}_A, \mathbf{r}_B) \{ \phi(r_{1A}) \psi(r_{2B}) - \phi(r_{2A}) \psi(r_{1B}) \},$$

where r_{iA} and r_{iB} are the distances of the valence electron from the nuclei A and B , respectively.

Adopting a device employed by Holstein (1952), we divide space by the median plane S through the midpoint of AB , perpendicular to AB . Let Γ_A be the left half-space containing nucleus A and let Γ_B be the right half-space containing nucleus B . Then

$$\begin{aligned} \{V(0|R) - V(1|R)\} & \int_{\Gamma_A} \int_{\Gamma_B} d\mathbf{r}_1 d\mathbf{r}_2 \chi_1(\mathbf{r}_1, \mathbf{r}_2; R) \chi_0(\mathbf{r}_1, \mathbf{r}_2; R) \\ & = \int_{\Gamma_A} \int_{\Gamma_B} d\mathbf{r}_1 d\mathbf{r}_2 \{\chi_1 H \chi_0 - \chi_0 H \chi_1\} \\ & = -\frac{1}{2} \int_{\Gamma_B} d\mathbf{r}_2 \int_{\rho} d\boldsymbol{\sigma}_1 \cdot (\chi_1 \nabla_1 \chi_0 - \chi_0 \nabla_1 \chi_1) \\ & \quad - \frac{1}{2} \int_{\Gamma_A} d\mathbf{r}_1 \int_{\rho} d\boldsymbol{\sigma}_2 \cdot (\chi_1 \nabla_2 \chi_0 - \chi_0 \nabla_2 \chi_1), \end{aligned}$$

the surface elements $d\boldsymbol{\sigma}_1$ and $d\boldsymbol{\sigma}_2$ being antiparallel. Substituting the assumed representations of χ_0 and χ_1 , we obtain

$$V(0|R) - V(1|R) = \frac{-\pi R S \phi(\frac{1}{2}R) \psi(\frac{1}{2}R)}{\Phi_A \Psi_B - \Phi_B \Psi_A},$$

where

$$\begin{aligned} S & = \int_{\Gamma_A + \Gamma_B} \psi(r_{2A}) \phi(r_{2B}) d\mathbf{r}_2, \\ \Phi_{A,B} & = \int_{\Gamma_{A,B}} |\phi(r_{1A})|^2 d\mathbf{r}_1, \\ \Psi_{A,B} & = \int_{\Gamma_{A,B}} |\psi(r_{2B})|^2 d\mathbf{r}_2. \end{aligned}$$

Since we require the atomic orbitals ϕ and ψ at large distances from the nucleus, we use the Coulomb approximation

$$\phi(r_A) = \frac{(2\alpha_A)^{\gamma_A}}{\gamma_A!} \left\{ \frac{\alpha_A}{4\pi\xi(\gamma_A)} \right\}^{\frac{1}{2}} r_A^{\gamma_A-1} \exp(-\alpha_A r_A),$$

where

$$\alpha_A = \sqrt{2I_A} = \gamma_A^{-1},$$

I_A atomic units being the ionization potential of atom A and $\xi(\gamma)$ is a function nearly equal to unity (cf. Seaton 1958) which we take to be unity. It is easy to show that when $(\alpha_A - \alpha_B)/(\alpha_A + \alpha_B)$ is small, the overlap integral S is given by

$$S \simeq \frac{4\pi(2\alpha_A)^{\gamma_A} (2\alpha_B)^{\gamma_B}}{(\alpha_A + \alpha_B)(\gamma_A + \gamma_B + 1)!} R^{\gamma_A + \gamma_B} \exp[-\frac{1}{2}R(\alpha_A + \alpha_B)].$$

For large values of R , Φ_A and Ψ_B tend exponentially to unity and Φ_B and Ψ_A tend exponentially to zero. Thus asymptotically

$$V(0|R) - V(1|R) = -N(\alpha_A, \alpha_B) R^{2\gamma-1} \exp(-\alpha R),$$

where

$$\gamma = \gamma_A + \gamma_B, \quad \alpha = \alpha_A + \alpha_B$$

and

$$N(\alpha_A, \alpha_B) = \frac{2\gamma \alpha_A^{2\gamma_A+1} \alpha_B^{2\gamma_B+1}}{\alpha \gamma_A! \gamma_B! (\gamma+1)!}.$$

Proceeding as for resonance charge transfer (cf. Bates & McCarroll 1962), we find that

$$\alpha p^* - (2\gamma - \frac{1}{2}) \ln p - \frac{1}{2} \ln \left(\frac{\pi^3 N^2}{2\alpha V^2} \right) - \frac{\gamma - \frac{1}{8}}{\alpha p^*} = 0$$

from which it follows that the spin-exchange cross-section can be written

$$Q_{\text{ex}}^{\frac{1}{2}} = a - b \ln E,$$

where a and b are constants depending only upon the ionization potentials of atoms A and B , and E is the energy of relative motion.

4. RESULTS AND DISCUSSION

The derived values of a and b , with energy measured in electron volts, are given in table 1 for all pairs selected from hydrogen, lithium, sodium, potassium, rubidium and caesium. A comparison of the cross-section for two hydrogen atoms with the

TABLE 1. VALUES OF a AND b IN UNITS OF 10^{-8} CM

| | H | Li | Na | K | Rb | Cs | |
|----|------|------|-------------------|-------|-------|-------|-----|
| H | 3.54 | 6.34 | 6.45 | 6.92 | 6.80 | 6.91 | (a) |
| | 0.22 | 0.27 | 0.28 | 0.29 | 0.29 | 0.30 | (b) |
| Li | — | 8.40 | 8.75 | 9.42 | 9.60 | 9.84 | (a) |
| | — | 0.38 | 0.38 ₅ | 0.41 | 0.41 | 0.42 | (b) |
| Na | — | — | 9.23 | 10.02 | 10.27 | 10.59 | (a) |
| | — | — | 0.39 | 0.40 | 0.41 | 0.42 | (b) |
| K | — | — | — | 10.92 | 11.25 | 11.64 | (a) |
| | — | — | — | 0.43 | 0.43 | 0.43 | (b) |
| Rb | — | — | — | — | 11.65 | 12.32 | (a) |
| | — | — | — | — | 0.43 | 0.40 | (b) |
| Cs | — | — | — | — | — | 12.48 | (a) |
| | — | — | — | — | — | 0.44 | (b) |

TABLE 2. SPIN-EXCHANGE CROSS-SECTIONS AT 540 °K IN UNITS OF 10^{-14} CM²

| | H | Li | Na | K | Rb | Cs |
|----|-----|-----|-----|-----|-----|-----|
| H | 0.2 | 0.5 | 0.5 | 0.6 | 0.6 | 0.6 |
| Li | — | 0.9 | 1.0 | 1.1 | 1.1 | 1.2 |
| Na | — | — | 1.1 | 1.2 | 1.3 | 1.4 |
| K | — | — | — | 1.5 | 1.5 | 1.6 |
| Rb | — | — | — | — | 1.6 | 1.8 |
| Cs | — | — | — | — | — | 1.9 |

accurate quantal calculations of Dalgarno & Henry (1964) shows that the simple formula underestimates by about 30 %. The approximations which led to it are less severe for the other atom pairs and 30 % can be accepted as an upper limit to the possible error.

Values of the spin-exchange cross-sections for a temperature of 540 °K are presented in table 2. They are in harmony with the experimental data and in

particular with the recent more precise measurements of Jarrett (1964) who reports a spin-exchange cross-section of $1.7 \times 10^{-14} \text{ cm}^2$ for Rb-Rb at 360°K and of Moos & Sands (1964) who report spin-exchange cross-sections of $2.0 \times 10^{-14} \text{ cm}^2$, $1.9 \times 10^{-14} \text{ cm}^2$ and $2.3 \times 10^{-14} \text{ cm}^2$ for ^{85}Rb , ^{87}Rb and ^{133}Cs at 540°K , the probable error being $\pm 20\%$. The predicted slow variation with temperature is consistent, within the experimental error, with the measurements of Jarrett and of Moos & Sands.

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