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Spin-orbit relaxation of $\text{Cl}(^2P_{1/2})$ and $\text{F}(^2P_{1/2})$ in a gas of H_2

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The authors present quantum scattering calculations of rate coefficients for the spin-orbit relaxation of $\text{F}(^2P_{1/2})$ atoms in a gas of H_2 molecules and $\text{Cl}(^2P_{1/2})$ atoms in a gas of H_2 and D_2 molecules. Their calculation of the thermally averaged rate coefficient for the electronic relaxation of chlorine in H_2 agrees very well with an experimental measurement at room temperature. It is found that the spin-orbit relaxation of chlorine atoms in collisions with hydrogen molecules in the rotationally excited state $j=2$ is dominated by the near-resonant electronic-to-rotational energy transfer accompanied by rotational excitation of the molecules. The rate of the spin-orbit relaxation in collisions with D_2 molecules increases to a great extent with the rotational excitation of the molecules. They have found that the H_2/D_2 isotope effect in the relaxation of $\text{Cl}(^2P_{1/2})$ is very sensitive to temperature due to the significant role of molecular rotations in the nonadiabatic transitions. Their calculation yields a rate ratio of 10 for the electronic relaxation in H_2 and D_2 at room temperature, in qualitative agreement with the experimental measurement of the isotope ratio of about 5. The isotope effect becomes less significant at higher temperatures. © 2007 American Institute of Physics. [DOI: 10.1063/1.2732751]

I. INTRODUCTION

The $\text{F}+\text{H}_2$ and $\text{Cl}+\text{H}_2$ systems have become model examples of chemical physics. The reaction of F with H_2 is a paradigm for exothermic abstraction reactions of atoms with diatomic molecules^{1,2} and the reaction of Cl with H_2 is a prototype of chemical reactions of chlorine with hydrocarbons,^{2,3} which play an important role in many atmospheric phenomena. The reactions of F and Cl with H_2 have therefore been studied theoretically and experimentally by many authors.^{1–58} The spin-orbit interaction in the ground electronic state of the halogen atoms gives rise to two fine structure energy levels $^2P_{1/2}$ and $^2P_{3/2}$. Quantum mechanical calculations have shown that the relative reactivity of the spin-orbit excited $\text{F}(^2P_{1/2})$ and $\text{Cl}(^2P_{1/2})$ atoms with hydrogen molecules is significantly reduced in comparison with the reaction probabilities of $\text{F}(^2P_{3/2})$ and $\text{Cl}(^2P_{3/2})$.^{1–31} This was in agreement with measurements of state-resolved reaction cross sections for fluorine⁵⁰ but disagreed with the experiments for chlorine.^{45,49,50} The disagreement has not yet been resolved and it is sometimes attributed to inaccuracies in the theoretical models of $\text{Cl}-\text{H}_2$ interactions.

The interactions of $\text{F}(^2P)$ and $\text{Cl}(^2P)$ with H_2 are characterized by three adiabatic interaction potentials and the reactions of $\text{F}(^2P_{1/2})$ and $\text{Cl}(^2P_{1/2})$ with H_2 occur at low temperatures through nonadiabatic transitions.³ The same interactions determine the dynamics of spin-orbit transitions in nonreactive collisions of halogen atoms with H_2 . The analysis of fine structure relaxation in prereactive $\text{F}(^2P)-\text{H}_2$

and $\text{Cl}(^2P)-\text{H}_2$ complexes may therefore elucidate the mechanisms of the chemical reactions and help resolve the disagreement with the experiment. Nonreactive collisions of $\text{F}(^2P_{1/2})$ with H_2 have been studied by several authors.^{13,14,21,31,59} Rigorous quantum mechanical calculations demonstrated that the spin-orbit relaxation in $\text{F}(^2P_{1/2})+\text{H}_2$ collisions is dominated by near-resonant energy transfer.^{21,31} This propensity for conservation of energy in electronic relaxation of $\text{F}(^2P_{1/2})$ has not been observed experimentally and may lead to yet another disagreement between theory and experiment. As most experimental measurements for the spin-orbit relaxation of the halogen atoms are performed in thermal gases,⁴⁴ it is necessary to extend the previous calculations to explore the effect of the near-resonant energy transfer on thermally averaged rate coefficients. The spin-orbit relaxation of $\text{Cl}(^2P_{1/2})$ in a gas of H_2 was studied in several experiments.^{60–65} These measurements yielded thermally averaged rate constants for total spin-orbit relaxation of $\text{Cl}(^2P_{1/2})$ at room temperature but provided no insight into the mechanisms of the electronic relaxation. Reznikov and Umanskii presented an analytical model of long-range interaction potentials that determine the spin-orbit relaxation in $\text{Cl}(^2P_{1/2})-\text{H}_2$ collisions.^{66,67} In a subsequent work,⁶⁸ the same authors used their model to calculate the rate constants for spin-orbit quenching of Cl atoms and found an agreement with one of the experimental data. These results provided mechanistic insights into the dynamics of nonadiabatic spin-orbit transitions; however, they were based

on several approximations and a more accurate quantum mechanical calculation is necessary to support the conclusions of Reznikov and Umanskii.⁶⁸

The adiabatic potentials and the nonadiabatic couplings describing the interactions of F and Cl with H₂ in the entrance reaction channel have been recently computed with high accuracy.^{1,48} In the present work, we employ these potentials to explore the nonadiabatic dynamics of the spin-orbit transitions in collisions of F(²P_{1/2}) and Cl(²P_{1/2}) atoms with H₂ and D₂ molecules. We calculate state-averaged rate coefficients for a comparison with the experimental data for chlorine and analyze the relative efficiency of the spin-orbit relaxation of fluorine and chlorine in H₂. We present a detailed comparison of the energy transfer mechanisms in collisions of F(²P_{1/2}) and Cl(²P_{1/2}) with H₂ and Cl(²P_{1/2}) with D₂. We find that the electronic relaxation of Cl(²P_{1/2}) in collisions with both H₂ and D₂ is dominated by resonant energy transitions.

II. THEORY

The theory for quantum calculations of X(²P)+H₂(¹Σ) collisions is based on the work by Baer,⁶⁹ Rebentrost and Lester,²¹ Alexander *et al.*,^{1,70,71} and Dubernet and Hutson.^{72,73} The total Hamiltonian of the X(²P)+H₂ system can be written in a.u. as follows:

$$\hat{H}_{\text{tot}} = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R - \frac{1}{2\mu_{\text{H}_2} r} \frac{\partial^2}{\partial r^2} r + \frac{j^2}{2\mu_{\text{H}_2} r^2} + \frac{l^2}{2\mu R^2} + V(r, R, \theta, \theta_a, \phi, \phi_a) + V_{\text{H}_2}(r) + \hat{V}_{\text{SO}}. \quad (1)$$

In this expression, R is the center-of-mass separation of the colliding particles, r is the interatomic distance in H₂, θ and ϕ specify the orientation of the diatomic molecule vector \mathbf{r} and θ_a and ϕ_a the orientation of the hole in the valence shell of the ²P atom with respect to the atom-molecule separation axis \mathbf{R} (see Ref. 72 for a detailed explanation of this notation), j is the rotational angular momentum of the diatomic molecule, l is the orbital angular momentum for the collision, μ is the reduced mass of the colliding particles, and μ_{H_2} is the reduced mass of the H₂ molecule. The term V denotes the potential for the X(²P)+H₂ interaction depending on all the Jacobi coordinates⁷² and V_{H_2} is the intramolecular potential for the vibrational motion of H₂. \hat{V}_{SO} is the spin-orbit interaction represented as

$$\hat{V}_{\text{SO}} = A \mathbf{L} \cdot \mathbf{S}, \quad (2)$$

where \mathbf{L} is the electronic orbital angular momentum and \mathbf{S} is the electronic spin angular momentum of the X(²P) atom. The constant A is related to the fine structure splitting Δ of the open-shell atom as $A = -2\Delta/3$.

The scattering wave function ψ^{JM} is expanded in terms of products of vibrational $\chi_v^j(r)$ and rotational $|jk\rangle$ wave functions of H₂, electronic functions $|L\lambda S\sigma\rangle$ of the X(²P) atom, and the Wigner rotation matrix elements as follows:

TABLE I. The energy of the rotational levels of H₂ and D₂ in units of cm⁻¹.

| j | H ₂ | D ₂ |
|-----|----------------|----------------|
| 0 | 0 | 0 |
| 1 | 118.7 | 59.8 |
| 2 | 354.2 | 179.0 |
| 3 | 712.0 | 357.1 |
| 4 | 1168.2 | 593.4 |
| 5 | 1780.1 | 886.8 |
| 6 | 2413.6 | 1235.9 |
| 7 | 3322.8 | 1639.4 |

$$\psi^{JM} = \frac{1}{R} \sqrt{\frac{2J+1}{4\pi}} \sum_{v,j,k,\lambda,\sigma} F_{vjkL\lambda S\sigma}^J(R) \chi_v^j(r) \times D_{M,k+\lambda+\sigma}^{J*}(\alpha_R, \beta_R, 0) |jk\rangle |L\lambda S\sigma\rangle, \quad (3)$$

where k , λ , and σ are the body-fixed projections of \mathbf{j} , \mathbf{L} , and \mathbf{S} , respectively, on the atom-molecule separation axis, J is the quantum number for the total angular momentum defined as the vector sum of \mathbf{j} , \mathbf{L} , \mathbf{S} , and \mathbf{l} , and α_R and β_R are the angles describing the orientation of the vector \mathbf{R} in the space-fixed coordinate system.

The substitution of the expansion [Eq. (3)] into the stationary Schrödinger equation with the Hamiltonian [Eq. (1)] leads to the following system of coupled differential equations for the expansion coefficients $F_{vjkL\lambda S\sigma}^J$:

$$\left[\frac{d^2}{dR^2} + k_{vj}^2 \right] F_{vjkL\lambda S\sigma}^J(R) = 2\mu \sum_{v',j',k',\lambda',\sigma'} \langle v'jk'L\lambda S\sigma | \hat{V} + \hat{V}_{\text{SO}} | v'j'k'\lambda' S\sigma' \rangle F_{v'j'k'\lambda' S\sigma'}^J(R) + \frac{l^2}{2\mu R^2} |v'j'k'\lambda' S\sigma' J\rangle F_{v'j'k'\lambda' S\sigma'}^J(R), \quad (4)$$

where $k_{vj}^2 = 2\mu(E - \epsilon_{vj})$, E is the total collision energy, and ϵ_{vj} are the rovibrational energies of the H₂ molecule. We calculate ϵ_{vj} by diagonalizing the Hamiltonian of the isolated diatomic molecule. The energies of the rotational energy levels of H₂ and D₂ used in our calculations are listed in Table I.

The matrix elements $V_{L\lambda S\sigma, L'\lambda' S'\sigma'} = \langle L\lambda S\sigma | \hat{V} | L'\lambda' S'\sigma' \rangle$ can be evaluated as described by Alexander *et al.*^{1,70,71} In order to obtain the matrices of the angular momentum and spin-orbit operators, we use the transformation

$$|j_a k_a\rangle = \sum_{\lambda, \sigma} |L\lambda S\sigma\rangle \langle L\lambda S\sigma | j_a k_a \rangle, \quad (5)$$

where j_a is the total electronic angular momentum of the A(²P) atom ($\mathbf{j}_a = \mathbf{L} + \mathbf{S}$), k_a is the projection of \mathbf{j}_a on the body-fixed quantization axis, and the symbol in the brackets is a Clebsch-Gordan coefficient. The spin-orbit Hamiltonian [Eq. (2)] is diagonal in the $|j_a k_a\rangle$ representation with the elements corresponding to the energies of the ²P_{1/2} and ²P_{3/2} spin-orbit states of the open-shell atom. The matrix of the l^2 operator can be evaluated in the $|jk\rangle |j_a k_a\rangle$ basis using the relation

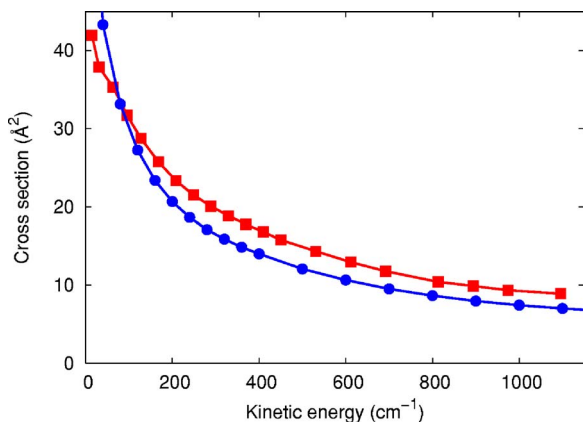


FIG. 1. Cross sections for the spin-orbit relaxation of $F(^2P_{1/2})$ in collisions with H_2 : (circles) this work and (squares) the results of Alexander *et al.* (Ref. 1).

$$l^2 = J^2 + j^2 + j_a^2 + 2j_{az}j_z - 2J_zj_z - 2J_zj_{az} + j_-j_{a+} + j_+j_{a-} - J_-j_{a+} - J_+j_{a-} - J_-j_+ - J_+j_-, \quad (6)$$

where J_z , j_{az} , and j_z are the operators that give the z component of J , j_a , and j , respectively, and J_{\pm} , $j_{a\pm}$, and j_{\pm} are the corresponding ladder operators. The body-fixed projection of the total angular momentum $\Omega = \lambda + \sigma + k$ is conserved in the absence of the Coriolis interaction, and states with large values of Ω play no role for transitions involving low rotational angular momenta of the diatomic molecule.^{1,74} We neglect states with $|\Omega| > 4$ in our basis set and perform the calculations as explained in Ref. 74.

III. RESULTS

We use the spin-orbit splitting constants $\Delta = 404 \text{ cm}^{-1}$ for F and $\Delta = 882 \text{ cm}^{-1}$ for Cl as recommended by NIST.⁷⁵ The cross sections are calculated for 101 kinetic energies in the interval from 1 to 4400 cm^{-1} and the total angular momenta $J = 0.5 - 80.5$ for $F(^2P_{1/2}) + H_2$ collisions, $J = 0.5 - 100.5$ for $Cl(^2P_{1/2}) + H_2$ collisions, and $J = 0.5 - 140.5$ for $Cl(^2P_{1/2}) + D_2$ collisions. The computation parameters were chosen to ensure the convergence of all integral cross sections to within 2%. We consider molecules only in the

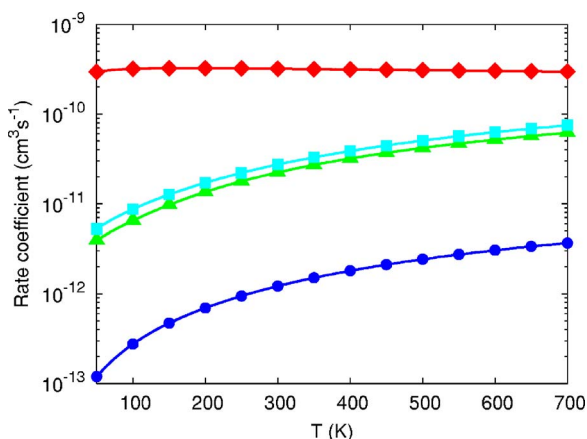


FIG. 2. Rate coefficients for the $F(^2P_{1/2}) + H_2(j)$ relaxation [Eq. (7)]: (diamonds) $j=0 \rightarrow j'=2$, (squares) $j=2 \rightarrow j'=2$, (triangles) $j=0 \rightarrow j'=0$, and (circles) $j=2 \rightarrow j'=0$.

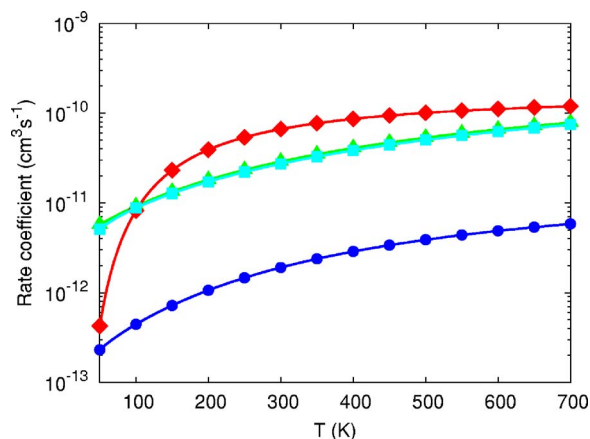


FIG. 3. Rate coefficients for the $F(^2P_{1/2}) + H_2(j)$ relaxation [Eq. (7)]: (diamonds) $j=1 \rightarrow j'=3$, (triangles) $j=1 \rightarrow j'=1$, (squares) $j=3 \rightarrow j'=3$, and (circles) $j=3 \rightarrow j'=1$.

ground vibrational state so we fixed the interatomic distance of both H_2 and D_2 at $r_0 = 1.448$ bohr and ignored the vibrational dependence of the wave functions in basis (3). We have verified by a full calculation including the vibrational dependence of the interaction potential that this approximation changes the rate constants for the spin-orbit relaxation of fluorine by less than 1.5%. The interaction potentials we used for the present calculations were analyzed in great detail by Alexander *et al.* in Figs. 1–5 of Ref. 1 for $F + H_2$ and by Klos *et al.* in Figs. 1–7 of Ref. 48 for $Cl + H_2$.

Our calculations ignore chemical reaction channels. The interactions of F and Cl atoms with H_2 molecules at short range are characterized by significant reaction barriers so this approximation should be accurate at low collision energies. Alexander *et al.* calculated cross sections for inelastic spin-orbit relaxation in $F(^2P_{1/2}) + H_2$ collisions using a rigorous quantum mechanical method including couplings to chemical reaction channels (see Fig. 9 of Ref. 1). In order to verify the accuracy of our approach, we repeated the calculations of Alexander *et al.*¹ The results shown in Fig. 1 demonstrate that our calculations are accurate to within 30% or better at all collision energies considered by Alexander *et al.* The activation barrier for the $Cl + H_2$ reaction is larger

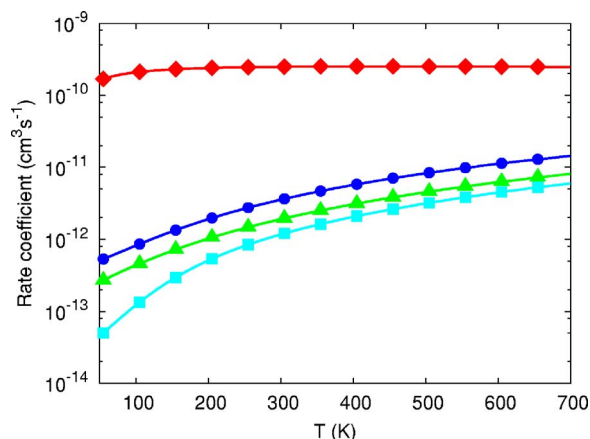


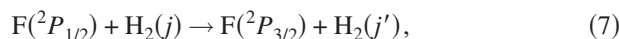
FIG. 4. Rate coefficients for the $Cl(^2P_{1/2}) + H_2(j)$ relaxation [Eq. (8)]: (diamonds) $j=2 \rightarrow j'=4$, (circles) $j=0 \rightarrow j'=2$, (triangles) $j=2 \rightarrow j'=2$, and (squares) $j=0 \rightarrow j'=0$.

TABLE II. Rate coefficients for the the $F(^2P_{1/2})+H_2$ relaxation [Eq. (7)] in units of $\text{cm}^3 \text{s}^{-1}$.

| T (K) | $j=0 \rightarrow j'=0$ | $j=0 \rightarrow j'=2$ | $j=2 \rightarrow j'=0$ |
|---------|-------------------------|------------------------|-------------------------|
| 50 | 0.394×10^{-11} | 0.295×10^{-9} | 0.120×10^{-12} |
| 100 | 0.651×10^{-11} | 0.319×10^{-9} | 0.276×10^{-12} |
| 150 | 0.972×10^{-11} | 0.324×10^{-9} | 0.471×10^{-12} |
| 200 | 0.135×10^{-10} | 0.324×10^{-9} | 0.695×10^{-12} |
| 250 | 0.178×10^{-10} | 0.322×10^{-9} | 0.946×10^{-12} |
| 300 | 0.224×10^{-10} | 0.320×10^{-9} | 0.122×10^{-11} |
| 350 | 0.271×10^{-10} | 0.317×10^{-9} | 0.151×10^{-11} |
| 400 | 0.320×10^{-10} | 0.314×10^{-9} | 0.181×10^{-11} |
| 450 | 0.370×10^{-10} | 0.311×10^{-9} | 0.212×10^{-11} |
| 500 | 0.420×10^{-10} | 0.308×10^{-9} | 0.243×10^{-11} |
| 550 | 0.470×10^{-10} | 0.305×10^{-9} | 0.275×10^{-11} |
| 600 | 0.520×10^{-10} | 0.302×10^{-9} | 0.306×10^{-11} |
| 650 | 0.570×10^{-10} | 0.299×10^{-9} | 0.338×10^{-11} |
| 700 | 0.620×10^{-10} | 0.297×10^{-9} | 0.369×10^{-11} |

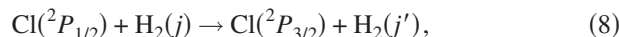
than for the $F+H_2$ reaction so our approach should be even more accurate for $Cl+H_2$ dynamics in the entrance reaction channel.

Figures 2 and 3 and Table II present the state-to-state rate coefficients for the spin-orbit relaxation of fluorine,



as functions of translational temperature and the initial and final rotational angular momenta of the molecule. The electronic relaxation is determined by the near-resonant energy transfer: the rate coefficient for the electronic transition accompanied with the rotational excitation of H_2 from $j=0$ to $j=2$ dominates by more than one order of magnitude. These results refine our previous data.³¹

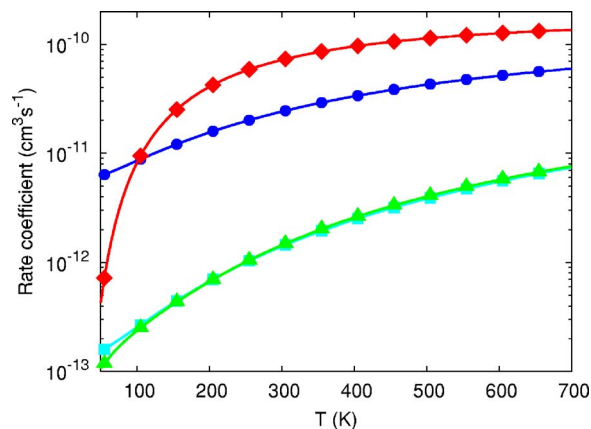
Figure 4 and Table III present the rate coefficients for the electronic relaxation of spin-orbit excited chlorine atoms,



in collisions with parahydrogen molecules. The process is dominated by the excitation of H_2 from $j=2$ to $j=4$, which results in a kinetic energy release of $\Delta E=68.3 \text{ cm}^{-1}$. Figure

TABLE III. Rate coefficients for the $Cl(^2P_{1/2})+H_2$ relaxation [Eq. (8)] in units of $\text{cm}^3 \text{s}^{-1}$.

| T (K) | $j=0 \rightarrow j'=2$ | $j=2 \rightarrow j'=2$ | $j=2 \rightarrow j'=4$ |
|---------|-------------------------|-------------------------|------------------------|
| 50 | 0.509×10^{-12} | 0.253×10^{-12} | 0.162×10^{-9} |
| 100 | 0.820×10^{-12} | 0.438×10^{-12} | 0.209×10^{-9} |
| 150 | 0.129×10^{-11} | 0.693×10^{-12} | 0.229×10^{-9} |
| 200 | 0.191×10^{-11} | 0.102×10^{-11} | 0.240×10^{-9} |
| 250 | 0.267×10^{-11} | 0.143×10^{-11} | 0.246×10^{-9} |
| 300 | 0.356×10^{-11} | 0.191×10^{-11} | 0.250×10^{-9} |
| 350 | 0.458×10^{-11} | 0.246×10^{-11} | 0.251×10^{-9} |
| 400 | 0.571×10^{-11} | 0.308×10^{-11} | 0.252×10^{-9} |
| 450 | 0.694×10^{-11} | 0.377×10^{-11} | 0.252×10^{-9} |
| 500 | 0.828×10^{-11} | 0.453×10^{-11} | 0.252×10^{-9} |
| 550 | 0.971×10^{-11} | 0.535×10^{-11} | 0.251×10^{-9} |
| 600 | 0.112×10^{-10} | 0.624×10^{-11} | 0.250×10^{-9} |
| 650 | 0.128×10^{-10} | 0.718×10^{-11} | 0.249×10^{-9} |
| 700 | 0.144×10^{-10} | 0.816×10^{-11} | 0.248×10^{-9} |

FIG. 5. Rate coefficients for the $Cl(^2P_{1/2})+H_2(j)$ relaxation [Eq. (8)]: (diamonds) $j=3 \rightarrow j'=5$, (circles) $j=1 \rightarrow j'=3$, (squares) $j=1 \rightarrow j'=1$, and (triangles) $j=3 \rightarrow j'=3$.

4 and Table III thus demonstrate that the relaxation of $Cl(^2P_{1/2})$ in collisions with rotationally excited H_2 molecules is also dominated by the near-resonant energy transfer. The comparison of Tables II and III shows that the rate coefficients for the near-resonant transitions in $Cl(^2P_{1/2})-H_2$ and $F(^2P_{1/2})-H_2$ collisions are very similar. This is remarkable, given that the spin-orbit splitting in chlorine is 2.2 times greater than the energy separation between the spin-orbit levels in fluorine.

Figure 5 and Table IV summarize the results for collisions of $Cl(^2P_{1/2})$ with ortho- H_2 . The rotational level structure of ortho- H_2 does not allow for the near-resonant energy transfer, and the overall rate of the electronic relaxation is much slower than in collisions with parahydrogen molecules. The process is dominated by two transitions in which H_2 is excited from $j=3$ to $j'=5$ and from $j=1$ to $j'=3$ (see Fig. 5).

The rate coefficients for the spin-orbit relaxation of chlorine in collisions with D_2 molecules are shown in Figs. 6 and 7. The spin-orbit relaxation of $Cl(^2P_{1/2})$ atoms in collisions with D_2 molecules in low rotational levels is much slower than in collisions with H_2 molecules. The minimization of energy change in the electronic-to-rotational energy transfer

TABLE IV. Rate coefficients for the $Cl(^2P_{1/2})+H_2$ relaxation [Eq. (8)] in units of $\text{cm}^3 \text{s}^{-1}$.

| T (K) | $j=1 \rightarrow j'=1$ | $j=1 \rightarrow j'=3$ | $j=3 \rightarrow j'=5$ |
|---------|-------------------------|-------------------------|-------------------------|
| 50 | 0.153×10^{-12} | 0.619×10^{-11} | 0.427×10^{-12} |
| 100 | 0.254×10^{-12} | 0.853×10^{-11} | 0.818×10^{-11} |
| 150 | 0.423×10^{-12} | 0.117×10^{-10} | 0.235×10^{-10} |
| 200 | 0.671×10^{-12} | 0.155×10^{-10} | 0.408×10^{-10} |
| 250 | 0.100×10^{-11} | 0.197×10^{-10} | 0.572×10^{-10} |
| 300 | 0.141×10^{-11} | 0.242×10^{-10} | 0.720×10^{-10} |
| 350 | 0.190×10^{-11} | 0.287×10^{-10} | 0.848×10^{-10} |
| 400 | 0.247×10^{-11} | 0.334×10^{-10} | 0.958×10^{-10} |
| 450 | 0.311×10^{-11} | 0.381×10^{-10} | 0.105×10^{-9} |
| 500 | 0.383×10^{-11} | 0.427×10^{-10} | 0.113×10^{-9} |
| 550 | 0.463×10^{-11} | 0.472×10^{-10} | 0.121×10^{-9} |
| 600 | 0.550×10^{-11} | 0.516×10^{-10} | 0.127×10^{-9} |
| 650 | 0.643×10^{-11} | 0.559×10^{-10} | 0.132×10^{-9} |
| 700 | 0.742×10^{-11} | 0.600×10^{-10} | 0.136×10^{-9} |

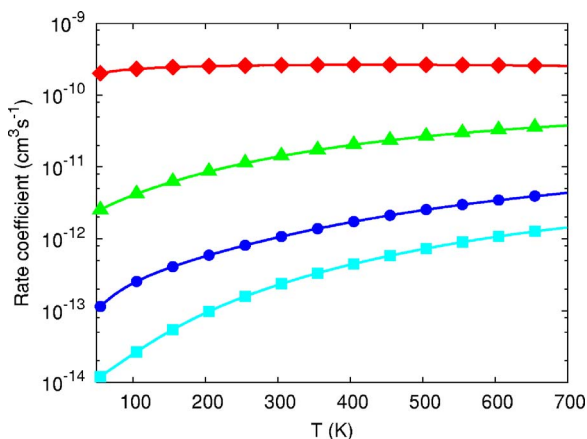


FIG. 6. Rate coefficient for the $\text{Cl}(^2P_{1/2})+\text{D}_2(j)$ relaxation: (diamonds) $j=6 \rightarrow j'=8$, (triangles) $j=4 \rightarrow j'=6$, (circles) $j=2 \rightarrow j'=4$, and (squares) $j=0 \rightarrow j'=2$.

in $\text{Cl}-\text{D}_2$ collisions requires significantly larger changes of the angular momentum of the molecule. Apparently, the anisotropy of the $\text{Cl}-\text{D}_2/\text{H}_2$ interaction potential is not strong enough to allow for large changes of the angular momentum. The rotational energy levels separate as the rotational angular momentum of the molecule increases and collisions with D_2 molecules in higher rotational states resemble collisions with H_2 molecules in low j levels. The electronic relaxation in $\text{Cl}(^2P_{1/2})-\text{D}_2$ collisions, therefore, becomes much more efficient when D_2 is rotationally excited.

In order to elucidate the propensities for the spin-orbit relaxation of fluorine and chlorine in a thermal hydrogen gas, we present in Table V the rate coefficients for the electronic relaxation in collisions with H_2 and D_2 in specific rotational levels summed over all final rotational states of the molecule. These results show that the overall spin-orbit relaxation of fluorine is most effective in collisions with H_2 molecules in the rotationally ground state $j=0$ and that the overall spin-orbit relaxation of chlorine is dominated by collisions with H_2 in the rotationally excited state $j=2$. Hydrogen molecules in a thermal gas populate a distribution of rotational energy levels with the probabilities given by

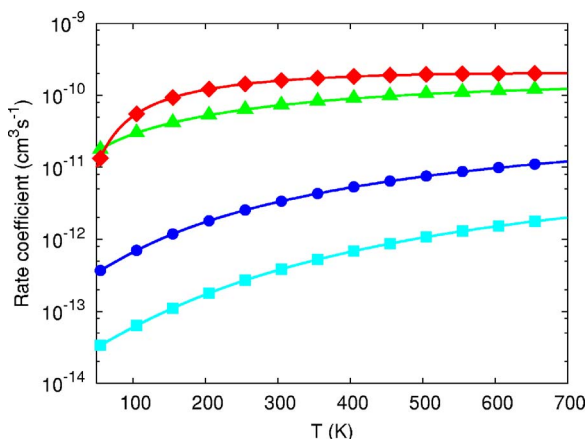


FIG. 7. Rate coefficient for the $\text{Cl}(^2P_{1/2})+\text{D}_2(j)$ relaxation: (diamonds) $j=7 \rightarrow j'=9$, (triangles) $j=5 \rightarrow j'=7$, (circles) $j=3 \rightarrow j'=5$, and (squares) $j=1 \rightarrow j'=3$.

TABLE V. Room temperature rate coefficients (in units of $\text{cm}^3 \text{s}^{-1}$) for spin-orbit relaxation of fluorine and chlorine in collisions with $\text{H}_2(j)$ summed over all final rotational states of the molecule.

| j | $\text{F}+\text{H}_2$ | $\text{Cl}+\text{H}_2$ | $\text{Cl}+\text{D}_2$ |
|-----|-------------------------|-------------------------|-------------------------|
| 0 | 0.342×10^{-9} | 0.511×10^{-11} | 0.548×10^{-12} |
| 1 | 0.953×10^{-10} | 0.256×10^{-10} | 0.114×10^{-11} |
| 2 | 0.368×10^{-10} | 0.252×10^{-9} | 0.151×10^{-11} |
| 3 | 0.308×10^{-10} | 0.735×10^{-10} | 0.355×10^{-11} |
| 4 | 0.291×10^{-10} | 0.129×10^{-10} | 0.141×10^{-10} |
| 5 | 0.291×10^{-10} | 0.219×10^{-11} | 0.729×10^{-10} |

$$P_j = g(j) \frac{(2j+1)e^{-\epsilon_j/k_B T}}{\sum_{j'} g(j')(2j'+1)e^{-\epsilon_{j'}/k_B T}}, \quad (9)$$

where $g(j)=1/4$ for H_2 in rotational levels with even j (parahydrogen), $g(j)=3/4$ for ortho- H_2 , $g(j)=2/3$ for D_2 in rotational levels with even j (orthodeuterium), and $g(j)=1/3$ for para- D_2 . A thermally averaged rate coefficient describing the rate of the spin-orbit relaxation of the halogen atoms in a gas of H_2 is expressed as

$$k(^2P_{1/2} \rightarrow ^2P_{3/2}) = \sum_j k_j P_j, \quad (10)$$

where k_j are the rate coefficients for collisions with hydrogen molecules initially in the rotational level with the angular momentum j summed over all final states of the molecule.

The results of Table V indicate that the thermally averaged rate coefficient for the spin-orbit relaxation of $\text{F}(^2P_{1/2})$ in H_2 should decrease somewhat with temperature at low temperatures and that the thermally averaged rate for the spin-orbit relaxation of chlorine should increase rapidly with temperature. Figure 8 presents the rate coefficients averaged over the distributions of the rotational states of the molecules as functions of temperature. We performed the calculations separately for the ortho- and paraisomers of H_2 and D_2 .

As expected based on Table V, the rate coefficient of Fig. 8 for the quenching of $\text{F}(^2P_{1/2})$ slightly decreases with temperature and passes through a minimum at $T \approx 150$ K. The rate coefficient for the spin-orbit relaxation of chlorine

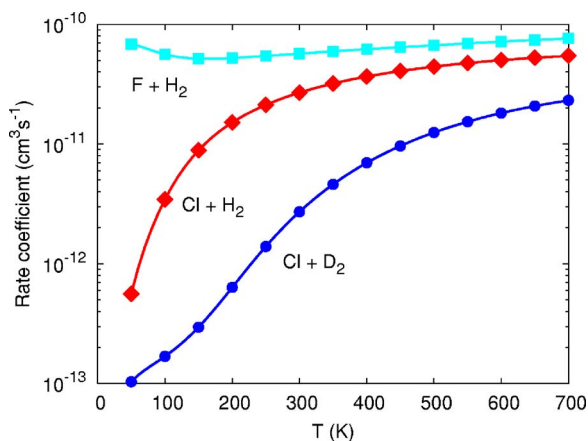


FIG. 8. Thermally averaged rate coefficients for the relaxation of (squares) $\text{F}(^2P_{1/2})$ by $\text{H}_2(j)$, (diamonds) $\text{Cl}(^2P_{1/2})$ by H_2 , and (circles) $\text{Cl}(^2P_{1/2})$ by D_2 .

TABLE VI. Room temperature rate coefficients (in units of $10^{-11} \text{ cm}^3 \text{ s}^{-1}$) for the $X(^2P_{1/2}) \rightarrow X(^2P_{3/2})$ ($X=\text{F}, \text{Cl}$) relaxation in a thermal gas of H_2 and D_2 .

| Reference | $\text{Cl}+\text{H}_2$ | $\text{Cl}+\text{D}_2$ | $\text{F}+\text{H}_2$ |
|-----------|------------------------|------------------------|-----------------------|
| This work | 2.687 | 0.2717 | 5.688 |
| Ref. 68 | 2.55 ^a | | |
| Ref. 60 | 0.7 | | |
| Ref. 61 | ≤ 0.06 | | |
| Ref. 62 | 5.0 ± 1.2 | 1.1 ± 0.3 | |
| Ref. 63 | 2.6 ± 0.7 | | |
| Ref. 64 | 8.0 ± 2.0 | 1.7 ± 0.4 | |
| Ref. 65 | 5.5 ± 1.6 | | |

^aValue obtained from Fig. 4 of Ref. 68.

increases rapidly at $T=50\text{--}250$ K and varies slowly at higher temperatures. The rate coefficient for the spin-orbit relaxation of chlorine in D_2 is much lower than the rate coefficient for the relaxation in H_2 at low temperatures. The two rates become similar at high temperatures due to the rapid increase of the relaxation rate in D_2 .

The Boltzmann-averaged rate coefficients for the relaxation of the spin-orbit excited states of Cl and F at room temperature are presented in Table VI in comparison with the experimental data for chlorine. Our calculation is in excellent agreement with the experimental measurement of Ref. 63. We note that the different experimental data differ from each other by a factor of 3. We find that the rate coefficient for the spin-orbit relaxation of $\text{Cl}(^2P_{1/2})$ in H_2 is about ten times larger than that for the relaxation in D_2 at room temperature. Although qualitatively correct, this is in quantitative disagreement with the experiments of Refs. 62 and 65 which yielded a smaller isotope ratio of 5. Our results are in remarkable agreement with the data of Reznikov and Umanskii at room temperature.^{67,68} The calculations of Reznikov and Umanskii are based on a model potential including the long-range quadrupole-quadrupole, dispersion and exchange interactions, the semiclassical approximation of nonadiabatic couplings, and the distorted wave method. Our more rigorous results support the conclusions of Reznikov and Umanskii and demonstrate that their model captures the main mechanism of the nonadiabatic transitions.

IV. SUMMARY

We have presented extensive quantum mechanical calculations of rate coefficients for the spin-orbit relaxation of $\text{F}(^2P_{1/2})$ and $\text{Cl}(^2P_{1/2})$ atoms in a gas of H_2 and D_2 molecules. We have found that the electronic relaxation of chlorine in collisions with both H_2 and D_2 molecules is dominated by the near-resonant electronic-to-rotational energy transfer when the molecules are rotationally excited. The spin-orbit relaxation of $\text{Cl}(^2P_{1/2})$ is most efficient when the rotational energy of H_2 molecules is transferred from the $j=2$ state to the $j=4$ level. Our calculation agrees very well with one of the experimental measurements and is within a factor of 3 of all recent experimental data for the relaxation of $\text{Cl}(^2P_{1/2})$ atoms in a thermal gas of H_2 at room temperature. This demonstrates that the interaction potential surfaces computed by Klos *et al.*⁴⁸ and the theoretical approach based

on the diabatic transformation of Baer,⁶⁹ Reberstrost and Lester,²¹ and Alexander *et al.*^{1,70,71} are accurate for the simulations of nonadiabatic dynamics in the entrance channel of the $\text{Cl}(^2P)+\text{H}_2$ chemical reaction. Alexander *et al.*³ used the same approach to study the effects of the spin-orbit interaction in the the $\text{Cl}(^2P)+\text{H}_2$ chemical reaction and the agreement of our results with the experimental data for nonreactive interactions thus supports their conclusions.

We have found that the rate coefficient for the spin-orbit relaxation of chlorine in a gas of H_2 is ten times larger than the rate coefficient for the relaxation in a gas of D_2 at room temperature. The experimentally observed ratio of the rate coefficients for the relaxation in H_2 and D_2 is about 5, so our results are in qualitative agreement with the experimental measurements of the isotope effect. We have found that the isotope effect is very sensitive to the temperature due to the significant role of molecular rotations in the nonadiabatic transitions. The spin-orbit relaxation in $\text{Cl}(^2P_{1/2})+\text{D}_2$ collisions becomes significantly faster when the molecule is rotationally excited and the thermally averaged rate coefficient for the spin-orbit relaxation in a gas of D_2 increases very rapidly with temperature. The isotope effect thus becomes smaller at high temperatures.

The spin-orbit relaxation of $\text{F}(^2P_{1/2})$ in a gas of H_2 is generally faster than the spin-orbit relaxation of $\text{Cl}(^2P_{1/2})$. The difference is most dramatic at low temperatures, where the electronic relaxation of fluorine is controlled by the near-resonant energy transfer and the near-resonant energy transfer in $\text{Cl}(^2P_{1/2})+\text{H}_2(j=0)$ collisions is not allowed. The rate coefficient for the electronic relaxation of fluorine decreases with temperature and passes through a minimum at $T \sim 150$ K, whereas the rate coefficient for the electronic relaxation of chlorine is a rapidly increasing function of temperature. The rates of the spin-orbit relaxation of fluorine and chlorine therefore appear to be of the same order of magnitude at temperatures between 200 and 350 K. This should be regarded as a coincidence as a result of the different mechanisms of the spin-orbit relaxation of fluorine and chlorine.

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