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COUPLED-CHANNEL STUDY

OF HALOGEN ($2p$) + RARE GAS ($1s$) SCATTERING

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ABSTRACT

Quantum mechanical coupled-channel (CC) scattering calculations are reported using realistic adiabatic potentials for the $2p + 1s$ interaction of F-Ar, F-Xe, and Cl-Xe. Differential cross sections $d\sigma/d\omega$ derived from a simple elastic approximation appropriate for large spin orbit interactions accurately reproduce all the gross features computed by the coupled-channel method. This finding supports the extraction of interaction potentials from laboratory differential cross sections $I(\theta)$ via an elastic analysis. Integral inter- and intramultiplet changing cross sections are expressed conveniently in terms of Grawert's $B(j, j'; g)$ coefficient. Information on the collision dynamics is extracted

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by following the partial wave dependence of selected $B(j,j';g)$.

Classical turning point analysis, based on the values of the large ℓ -waves for which these partial wave contributions $B_\ell(j,j';g)$ begin to rise above zero, leads to the conclusion that both intermultiplet and first order forbidden intramultiplet transitions are caused by a single localized nonadiabatic coupling region at the position of complex crossing of the $\Omega = 1/2$ adiabatic potentials. Small amplitude oscillations or perturbations in the CC calculated $d\sigma/d\omega$ and in the experimental $I(\theta)$ are thought to be examples of Stückelberg oscillations, though quantitative agreement between these quantities is not obtained. The energy dependence and interference structure of the computed $B(j,j;g)$ are briefly discussed, as is the approximation of the constant spin orbit interaction over the experimentally accessible range of internuclear distances.

I. Introduction

The effects of the interaction of different neighboring electronic states on collision processes is a well studied topic with a half century history. Reflecting this is a vast literature, and reviews are available.¹ Many of the experimental studies have utilized fluorescence detection and dealt with collisions involving $2P$ excited states of alkali atoms, with ground state rare gas atoms (RG), though other systems have been and are being investigated. Some recent examples of laboratory work can be found for depolarization of fluorescence (multipole cross sections),² fluorescence band shapes,³ high resolution spectroscopy (via fluorescence) on supersonic beam produced molecules,^{4,5} differential scattering cross sections by particle detection,⁶⁻¹² and integral inelastic cross sections via collision induced fluorescence.¹³⁻¹⁵ The studies always focus on the adiabatic potentials $V(R)$ as a function of internuclear distance R , and nonadiabatic coupling. Concomitant with this effort has been theoretical development, especially along semiclassical lines.^{7,16} A rigorous quantum mechanical treatment for $2P + 1S$ scattering has been developed by Mies¹⁷ and Reid,¹⁸ and theory now exists for the case of two $2P$ atoms or Σ state molecules.^{19,20}

Because they permit simple computational approaches, elastic collision models^{8,21} are especially useful in the analysis of experimental data. Discussion remains as to the accuracy of the models to predict total differential cross sections and integral inelastic cross sections. These formulations have focused on $2P$ collisions of alkali atoms or C^+ , systems with a single outer shell electron and small spin orbit splitting (Hund's case a or b). If the elastic approximation holds, it is possible

to extract valuable information on the interaction potentials by analyzing the laboratory differential cross sections $I(\theta)$.

There is considerable need for ground state interaction potentials for rare gas-halides RG-X due to the development of RG-X ultraviolet lasers and for the theory of termolecular recombination of these systems (see, e.g., citations in Ref. 11). Although these states are not easily accessible to standard optical spectroscopy, it is possible from crossed atomic beam scattering experiments to measure total $I(\theta)$ and, where the data are adequate, to extract the potentials from this data.

Though this study concerns again the familiar $2p + 1s$ interaction, the spin orbit splitting Δ is large (0.0501 eV for F and 0.109 eV for Cl), and a Hund's case c coupling holds. An elastic approximation appropriate to this coupling case has been employed for F-Xe and appears successful since a potential derived from scattering data corroborates a spectroscopically determined potential.¹⁰ If this approach is justified (and it appears it is) then accurate potentials can be obtained for ground state RG-X systems.¹⁰⁻¹² In turn, noting that both rigorous and approximate scattering models alike are quite sensitive to the $V(R)$ used, these realistic $V(R)$ can be the basis of more rigorous computations to yield detailed information unobtainable from an elastic model. Therefore, to both test this elastic approximation and obtain information on intra- and intermultiplet transitions among RG-X, quantum mechanical coupled-channel (CC) computations have been carried out employing the potentials derived from $I(\theta)$ measured in crossed atomic beams experiments.

II. Theory

A. Scattering

Neglecting mass polarization terms and nuclear spin, which should have a negligible effect on the collision dynamics, the scattering problem reduces for each total angular momentum J to solution of a set of coupled radial Schrödinger equations^{17,18}

$$\left[\frac{d^2}{dR^2} + k_j^2 - \frac{\ell(\ell+1)}{R^2} \right] F_{j\ell j'\ell'}^J(R) = \frac{2\mu}{h^2} \sum_{j''\ell''} V_{j\ell j''\ell''}^J(R) F_{j''\ell'' j'\ell'}^J(R) \quad (1)$$

Here μ is the reduced mass, $k_j^2 = 2\mu/h^2(E - E_j)$, and E is the total energy. The energy zero is chosen to be the $2P_{1/2} + 1S_0$ asymptote, so that $E_{j=1/2} = 0$ and $E_{j=3/2} = -\Delta$, and $E - E_j = E_{\text{rel}}$ which is the relative kinetic energy.

The notation for the quantum numbers involved is as follows:

j is the atomic angular momentum, m_j is the projection of j on a space fixed axis, Ω is the projection of j on the internuclear axis, ℓ is the nuclear orbital angular momentum, and J is the total angular momentum of the system. Primed (unprimed) quantities indicate final (initial) states. The molecular electronic states arising from the four-fold degenerate ground state $X(2P_{3/2}) + RG(1S_0)$ asymptote are the doubly degenerate I 1/2 (or X 1/2) and I 3/2 states. (In Hund's case b and a notation these are designated $2\Sigma^+$ and $2\Pi_{3/2}$, respectively.) From the doubly degenerate spin orbit excited manifold, $2P_{1/2} + 1S_0$, one also obtains the II 1/2 state ($2\Pi_{1/2}$ in Hund's case a). The 1/2, 3/2 are Ω values, and the

roman numerals indicate the energy ordering. Electronic states higher in energy than those already described are neglected because they lie considerably above the scattering energies investigated.

This set of coupled equations, Eq. (1), is derived in a space fixed frame and employs molecular adiabatic wavefunctions in constructing the total scattering wavefunction. Algebraically identical expressions for the interaction matrix elements $V_{j\ell j}^J$ have been evaluated by Reid¹⁸ and Mies¹⁷ following slightly different approaches. The matrix elements $V_{j\ell j}^J$ originate from the Born-Oppenheimer (BO) approximation and include the spin orbit interaction.¹⁷ In writing Eq. (1), BO radial and rotational coupling terms (i.e., terms describing the breakdown of the BO approximation) have been omitted (see Ref. 17). The BO radial coupling terms here are likely to be smaller than for the strongly bound $F + H^+$ where Mies reasons they are negligible. Perturbation theory at large R for RG-X shows that the rotational BO coupling terms is $O(R^{-8})$ versus $V_{j\ell j}^J O(R^{-6})$; while at smaller R , again following Mies' arguments for the stronger $F + H^+$ interaction, the rotational term will be small compared to the elements of $V_{j\ell j}^J$. Thus, these BO coupling terms have not been included.

The six open channels can be separated into two blocks according to parity,^{17,18} resulting in the solution of Eq. (1) for two sets of three coupled equations.

Equations (1) were solved numerically by the log-derivative integration technique²² to obtain the unitary and symmetric scattering matrices S^J , defined by the large R condition

$$F_{j\ell j'\ell'}^J \sim$$

$$\delta_{jj'} \delta_{\ell\ell'} \exp(-ik_j R - 1/2 \ell \pi) - \left(\frac{k_j}{k_{j'}} \right)^{1/2} S_{j\ell j'\ell'}^J$$

$$\times \exp(ik_{j'} R - 1/2 \ell' \pi) \quad (2)$$

Differential cross sections for $j \rightarrow j'$ transitions can be conveniently constructed from the S in the helicity representation²³ from

$$\frac{d\sigma(j \rightarrow j')}{d\omega} = (2j + 1)^{-1} \sum_{m_j = -j}^j \sum_{m_{j'} = -j'}^{j'} |f_{jm_j \rightarrow j'm_{j'}}(\theta)|^2 \quad (3)$$

where

$$f_{jm_j \rightarrow j'm_{j'}}(\theta) = (-1)^{j+j'} (2ik_j)^{-1} \sum_J (2J + 1) d_{m_{j'} m_j}^J(\theta)$$

$$\times \sum_{\ell\ell'} i^{\ell - \ell'} \begin{pmatrix} j' & J & \ell' \\ m_{j'} & -m_j & 0 \end{pmatrix} \begin{pmatrix} j & J & \ell \\ m_j & -m_{j'} & 0 \end{pmatrix}$$

$$\times [(2\ell' + 1)(2\ell + 1)]^{1/2} [S_{j\ell j'\ell'}^J - \delta_{jj'} \delta_{\ell\ell'}] ; \quad (4)$$

the bracketed $\begin{pmatrix} \end{pmatrix}$ quantities are Wigner 3j symbols. We followed Rose's phase convention²⁴ for the reduced rotation matrices.

The integral cross sections are evaluated by

$$\sigma(j \rightarrow j') = \frac{\pi}{(2j+1) k_j^2} \sum_{J \ell \ell'} (2J+1) |S_{j \ell j' \ell'}^J - \delta_{jj'} \delta_{\ell \ell'}|^2 \quad (5)$$

Integral cross sections with respect to specific m_j states

$\sigma(j m_j \rightarrow j' m_{j'})$ are related to the $\sigma(j \rightarrow j')$ by

$$\sigma(j \rightarrow j') = \sum_{m_j m_{j'}} \frac{\sigma(j m_j \rightarrow j' m_{j'})}{(2j+1)} \quad (6)$$

and are computed using the most irreducible form^{17,18b,25}

$$\sigma(j m_j \rightarrow j' m_{j'}) = \sum_g (j, j', g | m_j, -m_{j'}, m_j - m_{j'})^2 B(j, j'; g) \quad (7)$$

where g is a tensor order index, the $(j, j', g | m_j, -m_{j'}, m_j - m_{j'})$ is a Clebsch-Gordan coefficient, and the Grawert B coefficients are given by

$$B(j, j'; g) = \sum_{\ell} B_{\ell}(j, j'; g) \quad (8a)$$

$$B_{\ell}(j, j'; g) = \frac{\pi}{k_j^2} \sum_{\ell'} \left| \sum_J (-1)^{J+j'} (2J+1) \begin{Bmatrix} j & \ell & J \\ \ell' & j' & g \end{Bmatrix} T_{j \ell j' \ell'}^J \right|^2 \quad (8b)$$

where $\begin{Bmatrix} j & \ell & J \\ \ell' & j' & g \end{Bmatrix}$ is a 6j coefficient and $\underline{T} = \underline{I} - \underline{S}$. The 36 cross

sections are evaluated by 8 B coefficients (energy dependent). Multipole cross sections can be evaluated from the same coefficients.^{2,18b,25}

The simple elastic approximation used for Hund's case c coupling¹⁰ is given by

$$\frac{d\sigma_{el}(3/2 \rightarrow 3/2)}{d\omega} = 1/2 \left[\frac{d\sigma_{I \ 1/2}}{d\omega} + \frac{d\sigma_{I \ 3/2}}{d\omega} \right] , \quad (9a)$$

where the $d\sigma_i/d\omega$, $i \equiv I \ 1/2, I \ 3/2$, are computed following a single channel partial wave analysis. Consideration was given to an alternative expression, namely

$$\frac{d\sigma_{el}(3/2 \rightarrow 3/2)}{d\omega} = 1/2 \left| f_{I \ 1/2}(\theta) + f_{I \ 3/2}(\theta) \right|^2 , \quad (9b)$$

where the $f(\theta)$ are scattering amplitudes for a single channel. Equation (9b) was suggested by an analogy to symmetrical resonance scattering²⁶ where two adiabatic potentials (gerade and ungerade states) share a common asymptote. Equation (9b) was found to poorly represent the experimental $I(\theta)$ and CC calculated $d\sigma/d\omega$, and was not a good approximation. An objection to the analogy can be made on the following grounds. A physical picture for symmetric scattering is that transitions between the two states are constantly occurring over a very large range of internuclear distances. For the RG - X case, where $\Omega = 1/2$ and $3/2$ states correlate to the same $^2P_{3/2} + ^1S_0$ asymptote, the total electronic Hamiltonian is diagonal in Ω within the BO approximation (see following section). Equation (9b) should also not be applied to the $\Omega = 1/2$ potentials since the interstate coupling is found to be localized and fairly weak (see Section IV). A semiclassical analysis⁷ suited to this latter situation could be used for the $d\sigma/d\omega$ of the $\Omega = 1/2$ states but due to weak coupling, such complications are not warranted.

For comparison with the experimental $I(\theta)$, the relatively small $^2P_{1/2}$ component (~20%) present in the beam is included in the analysis by use of the expression

$$\frac{d\sigma_{el}}{d\omega} = 1/2(0.8) \left[\frac{d\sigma_{I \ 1/2}}{d\omega} + \frac{d\sigma_{I \ 3/2}}{d\omega} \right] + (0.2) \frac{d\sigma_{II \ 1/2}}{d\omega} \quad (10)$$

The approximation $\frac{d\sigma_{I \ 3/2}}{d\omega} \approx \frac{d\sigma_{II \ 1/2}}{d\omega}$ is made; this is suggested by theoretical evidence²⁷ that, with respect to each asymptote,

$V_{II \ 1/2} \approx V_{I \ 3/2}$ over the range of internuclear distances probed, and by the identical velocities of the $^2P_{1/2}$ and $^2P_{3/2}$ halogen atoms. The calculated $d\sigma_{el}/d\omega$ are transformed to the laboratory frame with velocity and angular averaging representative of the experimental configuration.

By varying the $V_{I \ 1/2}$ and $V_{I \ 3/2}$ potentials to achieve a best fit to the experimental $I(\theta)$, $V_{I \ 1/2}$ and $V_{I \ 3/2}$ are determined.

B. Interaction Potentials

The basis of the computations is the experimentally derived¹⁰⁻¹² $V_{I \ 1/2}$ and $V_{I \ 3/2}$, which are the BO potential curves, that is, the eigenvalues of the total electronic Hamiltonian over the range of R . Following Refs. 16(a,d) and 17, the total Hamiltonian is written as a sum of the electrostatic and spin orbit interactions:

$H_{tot} = H_{el} + H_{so}$. H_{so} is assumed R independent. The matrix elements

$$\langle R, j, \Omega | H_{tot} | R, j', \Omega' \rangle \equiv H_{jj'}^{\Omega} \quad (11)$$

are diagonal in Ω , and given by

$$H_{3/2, 3/2}^{3/2} = V_{II} - \Delta \quad (12a)$$

$$H_{1/2,1/2}^{1/2} = 1/3 V_{\Sigma} + 2/3 V_{\Pi} , \quad (12b)$$

$$H_{3/2,3/2}^{1/2} = 2/3 V_{\Sigma} + 1/3 V_{\Pi} - \Delta \quad (12c)$$

$$H_{1/2,3/2}^{1/2} = H_{3/2,1/2}^{1/2} = \frac{\sqrt{2}}{3} (V_{\Sigma} - V_{\Pi}) , \quad (12d)$$

where the V_{Σ} and V_{Π} are eigenvalues of H_{el} . The $\tilde{H}$ consists of 1×1 and 2×2 blocks with eigenvalues,

$$W(I \ 3/2) = V_{\Pi} - \Delta \quad (13a)$$

$$W(I \ 1/2) = 1/2 [V_{\Sigma} + V_{\Pi} - \Delta - D] \quad (13b)$$

$$W(II \ 1/2) = 1/2 [V_{\Sigma} + V_{\Pi} - \Delta + D] \quad (13c)$$

where

$$D = [(V_{\Sigma} - V_{\Pi})^2 + \Delta^2 - 2/3 \Delta (V_{\Sigma} - V_{\Pi})]^{1/2} . \quad (13d)$$

Thus, from the determined $V_{I \ 3/2}$, one obtains V_{Π} directly and V_{Σ} algebraically; the latter is given by

$$V_{\Sigma} = [2/3 \Delta V_{\Pi} + V_{\Pi} W(I \ 1/2) - \Delta W(I \ 1/2) - \{W(I \ 1/2)\}^2] / [V_{\Pi} - W(I \ 1/2) - 1/3 \Delta] . \quad (14)$$

$W(II \ 1/2)$ can be found from Eq. (13c).

To further specify the potential symbols used in relation to the $2p_{1/2} + 1s_0$ energy zero, one notes

$$W(I \ 3/2) = V_{\Pi} - \Delta = V_{I \ 3/2} - \Delta , \quad (15a)$$

$$W(I \ 1/2) = V_I \ 1/2 - \Delta \quad , \quad (15b)$$

$$W(II \ 1/2) = V_{II} \ 1/2 \quad , \quad (15c)$$

and in the limit of large R,

$$V_{II} = V_{\Sigma} = V_I \ 1/2 = V_I \ 3/2 = V_{II} \ 1/2 = W(II \ 1/2) = 0 \quad . \quad (15d)$$

In Reid's approach¹⁸ the molecular electrostatic potential is expanded in Legendre polynomials, dependent on the angle formed by the direction of the unpaired p orbital $\vec{r}$ with respect to the inter-nuclear position $\vec{R}$,

$$V(r,R) = \sum_i V_i(r,R) P_i(\vec{r} \cdot \vec{R}) \quad . \quad (16)$$

Only two terms contribute to the expansion giving'

$$V_{\Sigma} = V_0 + 2/5 V_2 \quad ; \quad V_{II} = V_0 - 1/5 V_2 \quad , \quad (17a)$$

or

$$V_0 = (V_{\Sigma} + 2 V_{II})/3 \quad ; \quad V_2 = 5/3(V_{\Sigma} - V_{II}) \quad . \quad (17b)$$

Substituting V_0 and V_2 into Eq. (13) gives

$$W(I \ 3/2) = V_0 - 1/5 V_2 - \Delta \quad (18a)$$

$$W(I \ 1/2) = (V_0 + 1/10 V_2 - \Delta/2) - D' \quad (18b)$$

$$W(II \ 1/2) = (V_0 + 1/10 V_2 - \Delta/2) + D' \quad (18c)$$

where

$$D' = \frac{1}{2} [25\Delta^2 - 10\Delta V_2 + 9V_2^2]^{1/2} . \quad (18d)$$

Alternatively, one has

$$V_0 = \frac{1}{3} [W(I \ 1/2) + W(II \ 1/2) + W(I \ 3/2) + 2\Delta] \quad (19a)$$

$$V_2 = \frac{5}{3} [W(I \ 1/2) + W(II \ 1/2) - 2W(I \ 3/2) - \Delta] . \quad (19b)$$

III. Results

A. Numerical Considerations

The convergence of the S was checked by varying the integration step size and end point. A step size of $1/(10k)$ (where k is the larger of the two values for the scattering channels) was used for the majority of computations. The integration starting point was kept at the origin and the end point fixed at $21 \text{ \AA}$ (however, see Section III-D).

Some computations focused on the fine structure transition, and for these the computations were carried out to a J determined as the value that gave convergence of the inelastic channels (S elements the size of 10^{-7}). For elastic scattering computations the maximum J was much larger and determined by the running sum of the elastic integral cross section not changing by more than ~ 1 part in 10^5 per J .

Integral cross sections calculated by different methods served as a consistency check in the present study. Agreement well within 1% was always found between $\sigma(j \rightarrow j')$ computed by direct summation (Eq. (5)), by numerical integration of the $d\sigma(j \rightarrow j')/d\omega$ (see Eqs. (3) and (4)),

$$\sigma = 2\pi \int_0^\pi \frac{d\sigma}{d\omega} \sin\theta d\theta \quad , \quad (20)$$

and by summation of the $\sigma(jm_j \rightarrow j'm_j')$ (see Eqs. (6)-(8)). In addition, for $2P_{3/2} + 1S_0$ scattering, the elastic approximation gave integral cross sections typically within 1% of the CC results. The elastic σ_{el} were computed from

$$\sigma_{el}(j = 3/2 \rightarrow 3/2) = 1/2(\sigma_{I\ 1/2} + \sigma_{I\ 3/2}) \quad (21)$$

where $\sigma_{I\Omega} \equiv \sigma$ for $\Omega = 1/2, 3/2$ is given by

$$\sigma = \frac{4\pi}{k^2} \sum_{\ell} (2\ell + 1) \sin^2 \eta_{\ell} \quad , \quad (22)$$

with phase shifts corresponding to the use of $V_{I\ 1/2}$ or $V_{I\ 3/2}$ and calculated by the Numerov or JWKB methods.

Due to very rapid diffractive oscillations for these systems of large reduced masses μ , at the higher energies studied the angular spacing for the scattering amplitude, Eq. (4), used in CC calculation of $d\sigma/d\omega$ had to be reduced to $1/8^\circ$ for $0^\circ \leq \theta \leq 90^\circ$ in order to obtain smooth representations of $d\sigma/d\omega$, and accurate σ by Eq. (20). At larger angles for the higher energies, and over the complete angular range for the lower energies, a $1/2^\circ$ spacing was satisfactory.

Comparisons of the $d\sigma/d\omega$ derived by the CC and elastic methods were carried out at energies chosen to coincide with nominal laboratory collision energies. At the temperature of the halogen atom beam sources, Boltzmann statistics predicts, for both F and Cl (coincidentally), ~22% $^2P_{1/2}$ component. The supersonic expansion yields both spin orbit states at the same velocity (same collision energy). So, in order to include the $^2P_{1/2}$ scattering, the CC computations were performed at two energies for any given elastic comparison. For example, to compare the F + Ar CC and elastically derived $I(\theta)$ for a laboratory relative collision energy E_{rel} of 0.108 eV, the CC equations were solved for $E = 0.108$ eV and 0.058 eV. From the first set of S^J , $d\sigma(1/2 \rightarrow 1/2, 3/2)/d\omega$

were obtained, while the second set of S^J , $d\sigma(3/2 \rightarrow 1/2, 3/2)/d\omega$ could be obtained. Actually, $d\sigma(3/2 \rightarrow 1/2)/d\omega$ was conveniently obtained by detailed balance

$$(2j + 1) k_j^2 \frac{d\sigma(j \rightarrow j'; k_j)}{d\omega} = (2j' + 1) k_{j'}^2 \frac{d\sigma(j' \rightarrow j; k_{j'})}{d\omega} \quad (23)$$

The contribution of the four cross sections to the total scattering was weighted according to j (0.78 for $j = 3/2$ and 0.22 for $j = 1/2$), and center-of-mass (CM) to laboratory transformations were performed for the elastic and two inelastic transitions to arrive at the CC derived $I(\theta)$. However, it is noted that $\sigma(j \rightarrow j')$ for $j \neq j'$ has a negligible contribution to $I(\theta)$.

Representative cases for comparison of the CC and elastically calculated $I(\theta)$ were taken to be: F + Xe at E_{rel} of 0.0915 and 0.456 eV; F + Ar at 0.0859, 0.108, and 0.481 eV; and Cl-Xe at 0.112 eV.

Two groups of CC computations for these systems were carried out. The first group of computations suffered from an error in V_0 , V_2 (or V_Σ , V_Π) because the equivalency $V_{II\ 1/2} = V_{I\ 1/2}$ was made (the proper treatment is described in Section (II-B)). Analysis showed this error affected the two $\Omega = 1/2$ potentials, deepening the II 1/2 potential well and making the I 1/2 well more shallow. The net effect, in the classically accessible region, was to alter the $\Omega = 1/2$ potentials by ~10%, with the exception of the F-Ar, Xe II 1/2 states which were altered by ~20% (a small absolute change).

These runs could be used to test the sensitivity of the dynamics to the molecular potentials.

It was found that the sensitivity to the assumed equivalency of potentials was greatest for Cl-Xe, the case in which the V_I $3/2$ is deepest; the second, proper set of computations showed an increase in the small $\sigma(1/2 \rightarrow 3/2)$ by nearly 80% for $E = 0.00282$ eV. The F-Ar, Xe systems showed a decrease in $\sigma(1/2 \rightarrow 3/2)$ of 40% at low energies and a decrease of ~20% at the highest energies, with the exception of a slight increase of $\sigma(1/2 \rightarrow 3/2)$ at the lowest energy ($E = 0.0359$ eV) for F-Ar. Thus $\sigma(1/2 \rightarrow 3/2)$ for these systems shows considerable sensitivity to the potentials.

For $d\sigma(3/2 \rightarrow 3/2)/d\omega$, only minor differences were found between the two groups of computations in the positions and shapes of the rainbow or orbiting oscillations. When the second group of computations was carried out correctly, it was found that $d\sigma(1/2 \rightarrow 1/2)/d\omega$ changed negligibly (for F-Ar, Xe), reflecting the small error in V_{II} $1/2$ introduced in the first runs. The calculations were performed for values of E appropriate for the experimental E_{rel} of the $^2P_{3/2}$ level ($E_{rel} = E + \Delta$). Because of this agreement for the rather structureless $d\sigma(1/2 \rightarrow 1/2)/d\omega$, the fact that only a 22% contribution to the $I(\theta)$ is involved, and the expense and effort involved in the CC computations, it was decided to forego repeating the computations for $E = E_{rel}$ for $^2P_{1/2}$ scattering with the exception of 0.108 eV for F-Ar displayed below. These $d\sigma(1/2 \rightarrow 1/2, 3/2)/d\omega$ from the first group of computations are used only in the CC derived $I(\theta)$ plots and only with small weighting, and in no way affect any conclusions.

Aside from the energies of the experimental comparison, CC computations at other energies were carried out for F-Ar and F-Xe to get a clearer trend for $\sigma(1/2 \rightarrow 3/2)$.

B. F-Xe

The potentials employed are shown in Fig. 1. Examples of some CC derived $d\sigma/d\omega$ are shown in Fig. 2 for the two elastic channels and a fine structure transition in the CM frame. Rainbow structure is clearly seen for $d\sigma(3/2 \rightarrow 3/2)/d\omega$. The $d\sigma(1/2 \rightarrow 1/2)/d\omega$ reflects the essentially repulsive II $1/2$ state. The fast diffractive oscillations are seen to occur over the same angular range for both angular distributions $d\sigma(3/2 \rightarrow 1/2, 3/2)/d\omega$; semiclassically, this indicates interference between different branches of the deflection function or quantum mechanically, multiple wavepacket interference. Another oscillatory structure is found in $d\sigma(3/2 \rightarrow 3/2)/d\omega$ that is in phase with the $d\sigma(3/2 \rightarrow 1/2)/d\omega$; these are undulations in the envelope of diffractive oscillations, which have only a small effect on the angular averaged results. Such oscillations are not found in the single channel calculations. The changing period of the oscillations in the fine structure transition $d\sigma/d\omega$ can be analyzed semiclassically⁹ and indicates that for nearly head on collisions (large Θ) the difference in interfering impact parameters is smaller than at larger impact parameters (small Θ). The size of the $d\sigma(1/2 \rightarrow 3/2)/d\omega$ is nearly constant for all Θ . At lower energy, $d\sigma(3/2 \rightarrow 1/2)/d\omega$ shows broad undulations and lowered intensity.

The calculated $d\sigma/d\omega$ were converted to the laboratory frame and

the results are shown in Fig. 3 for $E_{\text{rel}} = 0.456$ eV in arbitrary units. The CC and elastic calculated $I(\theta)$ are shown with and without angular averaging, and are displaced arbitrarily for clarity. All $I(\theta)$ presented in this work correspond to a single collision energy (one Newton diagram). In the experimental analysis (Ref. 10-12) many Newton diagrams contribute to the velocity averaging, and such comparisons with experimental data can be found in these references. Figure 4 shows an angularly averaged $I(\theta)$ comparison for $E_{\text{rel}} = 0.0915$ eV in which orbiting is present. Agreement between the CC and elastic $I(\theta)$ for both these collision energies is extremely good. Values of CC computed $\sigma(j \rightarrow j)$ are listed in Table I.

Integral cross sections for fine structure transitions in F-Xe have been computed previously by both semiclassical^{16d} and quantum mechanical²⁸ methods; however, they use quite different sets of potentials and large differences are found between the $\sigma(1/2 \rightarrow 3/2)$ reported in Refs. 16d, 28, and the present study. Table II lists $\sigma(1/2 \rightarrow 3/2)$ for a range of collision energies. The $\sigma(1/2 \rightarrow 3/2)$ rise steeply at low collision energies to a less rapid increasing rate at higher energies.

The $\sigma(jm_j \rightarrow j'm_j')$ can be evaluated from the $B(j,j';g)$ by Eq. (7). The squares of the Clebsch-Gordan coefficients in Eq. (7) have been tabulated elsewhere²⁹ for these quantum numbers. Table III presents the calculated $B(j,j';g)$. Note that $B(3/2,3/2;g \neq 0)$, which corresponds to $j = 3/2$ intramultiplet ($m_j \neq m_j'$) transitions decrease slightly at higher E . This suggests that the effectiveness of the coupling responsible for these transitions is weakly proportional to the collision time.

$B(j,j;g)$ for odd g are forbidden as first order processes³⁰ and show interstate coupling. It is therefore worthwhile to examine these more closely, as well as the $B(1/2, 3/2;g)$, to gain further insight on the dynamics of these transitions. Note that $B(1/2,1/2;1) \equiv \sigma(1/2,1/2 \rightarrow 1/2,-1/2)$, $B(1/2,3/2;2) \equiv \sigma(1/2,1/2 \rightarrow 1/2,-3/2)$, and $B(3/2, 3/2;3) \equiv \sigma(3/2,3/2 \rightarrow 3/2,-3/2)$.

With this in mind, B_ℓ was computed for each step of the ℓ summation in Eq. (8). Results for $B_\ell(1/2,1/2;1)$, $B_\ell(1/2,3/2;1)$, $B_\ell(1/2,3/2;2)$, and $B_\ell(3/2,3/2;3)$ are shown in Fig. 5 for a total $E = 0.0414$ eV, and in Fig. 6 for $E = 0.405$ eV; the maximum ℓ values computed were 340 and 650, respectively.

At both energies the $B_\ell(1/2,3/2;g)$ show an oscillatory interference behavior with slightly different frequency components for $g = 1,2$. Significant contributions to $B(1/2,3/2;2)$ extend to smaller ℓ . Note that $B_\ell(1/2,1/2;1)$ and $B_\ell(1/2,3/2;g)$ occur over the same region of ℓ but $B_\ell(1/2,1/2;1)$ shows a smooth structure overall, with a small oscillatory component superimposed for 0.405 eV with a slightly different frequency than $B_\ell(1/2,3/2;g)$. The $1/2,1/2 \rightarrow 1/2,-1/2$ transition at 0.405 eV shows stronger coupling to the $3/2$ manifold, suggesting a model where part of the incoming $j = 1/2$ plane wave splits off and follows a lower adiabatic potential before rejoining the $^2P_{1/2}$ manifold. The decay of these transitions at high ℓ values (≈ 73 for 0.0414 eV and ≈ 200 for 0.405 eV) characterizes the extent of the classically sampled region of coupling, and so demarks the assumed localized coupling by the turning point for each of these ℓ . (If the

coupling is not localized, these turning points will delimit the large R range of coupling.) Approximating the $V_{II\ 1/2}$ by its ϵ and r_m (found from Eq. (13c)) and the remaining analytic potential parameters of $V_{I\ 3/2}$, the scattering analysis at 0.0414 and 0.405 eV give classical turning points of 3.5-3.7 Å characteristic of the nonadiabatic coupling inducing the intermultiplet transitions.

Also shown in Figs. 5 and 6 are the $B_\ell(3/2,3/2;3)$. They are seen to increase at large ℓ and the large ℓ values where they decay ($\sim 105, 208$) yield a coupling limit of 3.4-3.7 Å by turning point analysis for both $V_{I\ 1/2}$ and $V_{I\ 3/2}$ at both 0.0915 and 0.456 eV. Note that while the $B(3/2,3/2;3)$ mildly decreases with increasing energy, the individual partial wave contributions to these $B(B_\ell)$ rather strongly decrease with increasing energy. Not shown are the oscillatory $B_\ell(3/2,3/2;1)$ which have the same large ℓ dependence as $B_\ell(3/2,3/2;3)$ but extend to somewhat smaller ℓ , and the oscillatory ℓ -wave contributions to $B(3/2,3/2;2)$ which are quite broad and extend to smaller and larger ℓ . The $B_\ell(1/2,1/2;0)$ and $B_\ell(3/2,3/2;0)$ have the largest range. They are oscillatory in the region of ℓ 's sampling the nonadiabatic coupling, and have a long smooth tail at large ℓ .

A final remark is made for F-Xe. In general the fine structure inelastic transitions can occur for $\ell' = \ell$ or $\ell \pm 2$. The $|S|^2$ were summed independently for these two channels, and a strong propensity for $\ell' = \ell \pm 2$ was found. The relative contributions to $\sigma(1/2 \rightarrow 3/2)$ for $\ell' = \ell \pm 2$ vary from 2.9:1 at 0.02 eV to 2.3:1 at 1 eV in a smooth fashion.

C. F-Ar

The potentials employed are shown in Fig. 7. Angular averaged CC and elastically derived $I(\Theta)$ are compared in Fig. 8 for $E_{\text{rel}} = 0.108$ eV and are in good accord. Similar agreement was obtained at 0.0859 eV and 0.481 eV. Note the low amplitude oscillations present in the $I(\Theta)$ derived from the CC $d\sigma/d\omega$ at wide angles; these are comparable to oscillations found in the data (see Sec. IV).

We list selected CC computed integral elastic cross sections in Table IV, and values of $\sigma(1/2 \rightarrow 3/2)$ in Table V. The $\sigma(1/2 \rightarrow 3/2)$ of F-Ar are smaller than those for F-Xe but show a similar energy dependence; the weaker attractive interaction for F-Ar is perhaps indicative of weaker nonadiabatic coupling.

The B coefficients are presented for various E_{rel} in Table VI. The overall trends are similar to F-Xe. Plots of $B_{\ell}(1/2, 1/2; 1)$, $B_{\ell}(1/2, 3/2; 1)$, $B_{\ell}(1/2, 3/2; 2)$ and $B_{\ell}(3/2, 3/2; 3)$ versus ℓ for $E = 0.0582$ eV (maximum $\ell = 300$) are shown in Fig. 9. The trends of these quantities versus ℓ at higher energies are qualitatively the same as F-Xe. Remarks about those B_{ℓ} coefficients not shown for F-Xe ($B_{\ell}(3/2, 3/2; 0, 1, 2)$ and $B_{\ell}(1/2, 1/2; 0)$) also apply here. Applying the turning point analysis used for F-Xe to the high ℓ damping of B_{ℓ} gives a strong coupling region in the vicinity of $3.1 \text{ \AA}$ ($\ell \approx 60$) for the intermultiplet and $^2P_{1/2}$ intramultiplet transitions and $3.1\text{--}3.2 \text{ \AA}$ ($\ell \approx 84$) for the $^2P_{3/2}$ intramultiplet transitions, again giving a common value for the region of nonadiabatic coupling between the $^2P_{1/2}$ and $^2P_{3/2}$ manifolds.

EPR linewidth measurements^{31c} have been performed on F-Ar. From a semiclassical straight line trajectory model^{31a,b} intramultiplet

cross sections were obtained from the linewidths. Plots of the B_ℓ coefficients show the model inadequately represents the CC computed transitions; deficiencies of the model have been noted previously.^{31d,e} For the $^2P_{3/2}$ manifold no CC computations were carried out to permit direct comparison with the EPR study at 300°K; however, Table VI shows the slow variation of $B(3/2,3/2;1,2,3)$ with energy. The listed values 0.0359 and 0.0582 eV, for the $^2P_{1/2}$ case are in the energy range for comparison with this gas cell experiment. The comparisons with the EPR derived cross sections are poor. The extrapolated CC values for the transitions $^2P_{3/2}|m_j| = |3/2| \rightleftharpoons |1/2|$ are about a factor of two larger than given by Ref. 31c, while the CC values for the $^2P_{3/2}|m_j| = 1/2 \rightleftharpoons -1/2$ cross sections are about a factor of three smaller, and the CC values for the $^2P_{1/2}|m_j| = 1/2 \rightleftharpoons -1/2$ cross sections are about a factor of ten smaller. Considering the inadequacy of the model, we conclude that the cross sections of Ref. 31c do not provide a good test of the present calculations.

Four further tests to probe the sensitivity of the scattering cross sections to the $V(R)$ were carried out for $F + Ar$ at 0.0359 and 0.0582 eV. The potentials $V_{I\ 3/2}$ or $V_{I\ 1/2}$ were altered by changing one or two of the key parameters (ϵ , r_m , and β) of the MMSV analytic potential form by ~20%. The main interest was to see if the wide angle $d\sigma/d\omega$ oscillations could be amplified. (One other test equated the two C_6 constants--this had virtually no effect on any of the cross sections.) It was found that the oscillations could not be amplified, though they could be damped. One interesting case was found when the

$V_{I\ 1/2}$ β_1 parameter was increased from 4.3 to 5.3. This increased the $\sigma(1/2 \rightarrow 3/2)$ by a little more than a factor of two, with a slight decrease in $\sigma(1/2, 1/2 \rightarrow 1/2, -1/2)$, and the wide angle oscillations were damped. The other potential variations had comparatively minor effect.

Finally, the propensity for $\ell' = \ell \pm 2$ for the $\sigma(1/2 \rightarrow 3/2)$ was found by the channel ratios 2.9:1 at 0.0359 eV to 2.2:1 at 0.431 eV, changing in a smooth fashion.

D. Cl-Xe

The potentials employed for this systems are shown in Fig. 10. The CC computations were carried out using tentative fits to the data; subsequently, improved fits to the data were found, and the recommended Cl-Xe $V_{I\ 1/2}$ and $V_{I\ 3/2}$ are contained in Ref. 12. However, the $V(R)$ used here are close to the final values and the scattering cross sections should not differ markedly. The $V(R)$ used here will provide a good test of the elastic approximation for $I(\theta)$. For reference the MMSV parameters used here are given (analytic form is listed in Ref. 10): for the $V_{I\ 1/2}$, $\epsilon = 0.0304$ eV, $r_m = 3.18$ Å, $\beta_1 = 5.5$, $\beta_2 = 3.6$, $X_1 = 1.237$, $X_2 = 1.750$, $C_6 = 80.7$ eV·Å⁶, and $C_8 = 620$ eV·Å⁸; for the $V_{I\ 3/2}$, $\epsilon = 0.0147$ eV, $r_m = 4.10$ Å, $\beta_1 = 7.6$, $\beta_2 = 6.6$, $X_1 = 1.105$, $X_2 = 1.500$, $C_6 = 85.0$ eV·Å⁶, and $C_8 = 620$ eV·Å⁸.

To assure convergence of the elastic channels for this system a maximum J of 548.5 was used, which together with very low $E = 0.00282$ eV necessitated moving the final integration point, conservatively, to 100 Å.

A comparison of $I(\theta)$ computed by CC and elastic methods for $E_{rel} = 0.112$ eV is shown in Fig. 11. Agreement is good, though not quite as

close as for the F systems. The much more attractive Cl-Xe van der Waals $V_{I\ 3/2}(V_{II})$ is likely responsible for the slightly poorer agreement. Note some perturbation of the CC diffractive oscillations, and small oscillations in the wide angle $d\sigma/d\omega$ though the inelastic cross section is very small.

The $\sigma(1/2 \rightarrow 1/2)$ at $E_{rel} = 0.00282$ eV is $717.5 \text{ \AA}^2$, $\sigma(3/2 \rightarrow 3/2)$ at 0.112 eV is $403.7 \text{ \AA}^2$, $\sigma(1/2 \rightarrow 3/2) = 7.78 \text{ E-5 \AA}^2$ at 0.00282 eV, and the ratio of the $\ell' = \ell \pm 2$ to $\ell' = \ell$ channels for $\sigma(1/2 \rightarrow 3/2)$ is 3.0. Though the total energy here is just above zero, in general the $\sigma(1/2 \rightarrow 3/2)$ are expected to be smaller than for F-Ar, Xe due to the larger spin orbit splitting Δ of Cl, but this study does not probe this trend. To get an idea of the size of the $^2P_{3/2}$ intramultiplet transitions, and for completeness, the B coefficients are listed in Table VII.

Concerning the $\sigma(1/2 \rightarrow 3/2)$, the collision energy is just above threshold for the $3/2 \rightarrow 1/2$ transition (the $1/2$ channel is barely open) and this is well inside the orbiting regime for $V_{II\ 1/2}$. Consequently, cross sections pertaining to the $j = 1/2$ level should not be considered indicative of a large energy range, though $j = 3/2$ manifold intramultiplet transitions will be indicative of the thermal energy range.

Figure 12 presents selected B_ℓ as a function of ℓ . The B_ℓ relating to $j = 1/2$ are small in magnitude and show resonances probably associated with the close approach of the centrifugal barrier to E. Penetration through the centrifugal barrier to quasibound levels will

give rise to the observed structure. This seems to be the case as a turning point analysis for the $V_{II\ 1/2}$ at 0.00282 eV (again in the fashion employed for F-Xe) showed that for $\ell = 48$ the centrifugal barrier reached E. The previous turning point (for $\ell = 47$) was 3.75 Å, while at a few higher ℓ values the turning point was ~ 7 Å. Thus the turning point analysis can only bracket the coupling region, and shows why the ℓ decay of the $B_\ell(1/2, j'; g)$ is so sudden. The 0.112 eV analysis for the $V_{I\ 1/2}$ and $V_{I\ 3/2}$ give a common turning point of ~ 4.0 Å using $\ell \approx 165$ for the $B_\ell(3/2, 3/2; 3)$.

IV. Discussion

The close agreement between the $I(\theta)$ computed by the CC and elastic methods shows that the simple single channel approach to these RG-X three channel scattering problems is useful for extracting realistic $V(R)$ from experimental $I(\theta)$. Use of realistic $V(R)$ then makes the coupled-channels calculation meaningful for comparison or prediction of experimental quantities. It is difficult to assess how widely applicable this elastic method is to other electronic open shell systems when the spin orbit splitting is not as large as for the RG-X systems studied here. Certainly at hyperthermal energies where higher electronic states may become strongly coupled, the approximation is expected to deteriorate. We find poorer agreement between $I(\theta)$ computed by elastic and CC methods for Cl-Xe than for the F-RG systems. The Br- and I-RG systems, likely to have comparable and non-negligible attractive $V_{I\ 1/2}$ and $V_{I\ 3/2}$, probably will have their scattering less well represented by Eq. (9a), but sufficiently approximated to allow valid $I(\theta)$ analysis. Useful application to nonhalogen scattering with electronic states in qualitative resemblance to those here remains to be seen, as does that for strongly chemically bound systems. Of course, the more electronic states involved, the more smearing will appear in $d\sigma/d\omega$.

The elastic models (see Ref. 21 and references cited therein) previously used for small spin orbit coupling rest on the assumption that during the collision the electron orbital angular momentum and spin become uncoupled, and that coupling is weak between the adiabatic

states of the electrostatic electronic Hamiltonian. The physical meaning of the elastic analysis used here is that the electron orbital and spin angular momentum remain coupled throughout the collision, and coupling is weak between the adiabatic states of the total electronic Hamiltonian including spin orbit interaction.

An early motivation for this study was a desire to answer the question of the meaning of some small amplitude oscillations in the experimental $I(\theta)$; this is a small effect under scrutiny. The data are often ambiguous and possibly the random error analysis may not be giving reliable uncertainties, yet, at least for F-Ar, CC derived $I(\theta)$ are in semiquantitative agreement with the data as shown in Fig. 13. Remaining disagreement could rest in the data itself, insufficiently accurate $V(R)$, or in the assumptions used in carrying out the CC computations. The latter include possible underestimation of coupling to electronic states a few eV distant, underestimates of the BO coupling terms, and neglect of nuclear spin, though these all seem unlikely. Perhaps a more probable error is the assumption that the spin orbit interaction is constant over the internuclear distances probed by the scattering, especially for the anomalous F-Xe system (see discussion in Ref. 11). More efforts directed toward calculating the molecular spin orbit interaction from first principles is needed.

Plots of selected $B_\ell(j,j';g)$ versus ℓ reveal information about the collision dynamics. The $B_\ell(1/2,1/2;1)$ have the same range of ℓ contribution as the $B_\ell(1/2,3/2;g)$ supporting a common mechanism. Yet the lack of oscillations found in the low energy $B_\ell(1/2,1/2;1)$ and the

appearance of a minor oscillatory component at higher energy have been a surprising contrast to the $B_{\ell}(1/2, 3/2; g)$ oscillatory structure. This has prompted a suggestion that for $j = 1/2$ intramultiplet transitions at higher energies, in addition to the virtual transitions to the $^2P_{3/2}$ manifold, true double passage transitions out of and back to the $^2P_{1/2}$ manifold are occurring.

It is likely that nonadiabatic coupling in these systems is localized.³² The local ℓ wave dependence of the critical B coefficients support this as follows. The classical turning point analysis employed for the large ℓ decay of $B_{\ell}(j, j; g)$ for odd g , and $B_{\ell}(1/2, 3/2; g)$ has pointed to a common nonadiabatic coupling region for both inter- and intramultiplet transitions. This analysis is approximate, mostly due to the somewhat arbitrary choice of ℓ wave cut-off and approximate form of $V_{II\ 1/2}$, but the derived values probably are accurate as seen by the agreement of the turning points found for the adiabatic potentials at more than one energy for F-Ar, Xe, and the ability to explain the sharp ℓ cut-off for Cl-Xe. The critical turning points occur where the $V_{I\ 1/2}$ and $V_{I\ 3/2}$ splitting is still small. Undoubtedly the best explanation of this phenomena was given in 1932 by Stückelberg.³³ The nonadiabatic coupling is localized at where the adiabatic curves cross, and, here, this occurs in the complex plane for the $\Omega = 1/2$ adiabatic potentials, with the real R' component determined by

$$V_{\Sigma} - V_{II} = -\Delta/3 \quad . \quad (24)$$

For the potential employed here, to the nearest 0.1 Å, for F-Xe $R' = 3.6$ Å, for F-Ar 3.0 Å, and for Cl-Xe 3.7 Å. The coincidence of

these values with those of the turning point analysis of the fully quantum mechanical results is not accidental (and employing the $V_{I\ 3/2}$ in the analysis is not warranted). The small $I(\theta)$ oscillations observed in the laboratory and computed by the CC method should properly be termed Stückelberg oscillations.³⁴ It is also noteworthy that $d\sigma/d\omega$ perturbations appear for Cl-Xe even though Δ is much larger for Cl than for F, and the $\sigma(1/2 \rightarrow 3/2)$ is very small for the energy studied. Further study is needed to understand more fully the role of the complex V and R planes in molecular interactions.

V. Summary and Conclusions

Coupled-channel scattering calculations have been carried out in the thermal energy range using realistic interaction potentials for F-Xe, F-Ar, and Cl-Xe. These calculations support, by differential cross section comparisons, an elastic scattering model appropriate to Hund's case c, by which the $V(R)$ have been derived. The CC derived $d\sigma/d\omega$ show perturbations due to nonadiabatic coupling, in qualitative or semiquantitative agreement with experimental¹⁰⁻¹² $I(\theta)$. These are assumed to be Stückelberg oscillations based on the consistent agreement between classical turning points derived from the $B_\ell(j,j;g)$ for odd g , and $B_\ell(1/2,3/2;g)$ (intra- and intermultiplet transitions) decay as a function of nuclear orbital angular momentum and the real component of the complex crossing point between the $\Omega = 1/2$ adiabatic potentials. The strong positive energy dependence of $\sigma(1/2 \rightarrow 3/2)$ and $\sigma(1/2,1/2 \rightarrow 1/2,-1/2)$ indicate an ability to reach this complex crossing with enough momentum to pass through the crossing before adiabatic relaxation. On the other hand, the $^2P_{3/2}$ integral intramultiplet transitions show a weak negative energy dependence and a strong negative energy dependence for individual partial wave contributions even though they also are characterized by the same localized nonadiabatic crossing.

The question of the accuracy of approximating the molecular spin orbit coupling by the atomic value over a substantial range of internuclear distances is raised, especially for the Xe systems.

This study will be useful for future guidance for experimental investigation of Stückelberg oscillations. Though the currently available data for RG-X systems does not have sufficient resolution to provide detailed analysis of these oscillations, in principle it is shown that well resolved Stückelberg oscillations are a sensitive probe of the molecular potentials and interstate coupling, and further careful investigation is warranted.

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Table I. Elastic Integral Cross Sections in $\text{\AA}^2$ for F-Xe at Relative Collision Energies E_{rel} .

$E_{\text{rel}}(\text{eV})$	j	$\sigma(j \rightarrow j)$
0.0414	1/2	311.1
0.405	1/2	207.2
0.0915	3/2	241.7
0.456	3/2	188.2

Table II. F-Xe Fine Structure Transition Integral Cross Sections

$E \text{ (eV)}$	$\sigma(j = 1/2 \rightarrow 3/2) (\text{\AA}^2)$
0.020	0.00506
0.0414	0.0197
0.150	0.204
0.300	0.715
0.405	1.088
0.600	1.897
0.800	2.675
1.000	3.453

Table III. $B(j, j'; g)$ in $\text{\AA}^2$ for F-Xe at Relative Collision Energies E_{rel}

E_{rel} (eV)	$j \rightarrow j'$		$g = 0$	1	2	3
0.0141	1/2	1/2	6.22E+2	2.21E-2		
0.0414	1/2	3/2		3.62E-4	7.64E-3	
0.0915	3/2	3/2	8.15E+2	1.23E+1	2.09E+1	1.40E0
0.405	1/2	1/2	4.13E+2	3.40E-1		
0.405	1/2	3/2		9.57E-2	3.78E-1	
0.456	3/2	3/2	6.29E+2	1.13E+1	1.68E+1	8.88E-1

Table IV. Integral Elastic Cross Sections in $\text{\AA}^2$ for F-Ar at Relative Collision Energies E_{rel} .

E_{rel} (eV)	j	$\sigma(j \rightarrow j)$
0.108	1/2	175.4
0.431	1/2	130.2
0.108	3/2	165.9
0.456	3/2	130.7

Table V. F-Ar Fine Structure Changing
Integral Cross Sections

E (eV)	$\sigma(1/2 \rightarrow 3/2) (\text{\AA}^2)$
0.0359	0.00122
0.0582	0.00529
0.108	0.0349
0.200	0.128
0.300	0.314
0.431	0.700

Table VI. $B(j, j'; g)$ in $\text{\AA}^2$ for F-Ar at Relative Collision
Energies E_{rel}

E_{rel} (eV)	$j \rightarrow j'$		$g = 0$	1	2	3
0.0359	1/2	1/2	3.70E2	1.14E-2		
0.0359	1/2	3/2		3.87E-5	4.62E-4	
0.0859	3/2	3/2	5.82E2	5.82E0	1.57E1	9.67E-1
0.0582	1/2	1/2	3.17E2	2.22E-2		
0.0582	1/2	3/2		2.83E-4	1.94E-3	
0.108	3/2	3/2	5.65E2	5.89E0	1.47E1	9.37E-1
0.108	1/2	1/2	3.51E2	5.49E-2		
0.108	1/2	3/2		2.18E-3	1.26E-2	
0.158	3/2	3/2	5.50E2	6.14E0	1.42E1	9.06E-1
0.431	1/2	1/2	2.59E2	3.57E-1		
0.431	1/2	3/2		1.03E-1	2.18E-1	
0.481	3/2	3/2	4.34E2	7.24E0	1.20E1	8.87E-1

Table VII. $B(j,j';g)$ in $\text{\AA}^2$ for Cl-Xe at Relative Collision Energy E_{rel}

E_{rel} (eV)	$j \rightarrow j'$		$g = 0$	1	2	3
0.00282	1/2	1/2	1.43E3	1.10E-3		
0.00282	1/2	3/2		4.20E-7	3.08E-5	
0.112	3/2	3/2	1.44E3	1.18E1	2.50E1	1.25E0

Figure Captions

Fig. 1. The F-Xe interaction potentials for the I 1/2, I 3/2, and II 1/2 states (—) are shown in eV vs Å. The Π and Σ potentials (- - -) governed solely by electrostatic forces, are also shown in eV. The derived V_0 and V_2 (—) are given in hartree vs Å. The energy zero is the $2p_{1/2} + 1s_0$ asymptote.

Fig. 2. Absolute ($\text{\AA}^2$) differential cross sections for F-Xe in the center-of-mass frame. (a) $j = 1/2 \rightarrow 1/2$ at relative collision energy $E_{\text{rel}} = 0.406$ eV. This curve has been displaced upwards one order of magnitude for clarity. (b) $j = 3/2 \rightarrow 3/2$ at $E_{\text{rel}} = 0.456$ eV. (c) $d\sigma(1/2 \rightarrow 3/2)/d\omega$ at $E_{\text{rel}} = 0.406$ eV ($= (0.455) d\sigma(3/2 \rightarrow 1/2)/d\omega$ at $E_{\text{rel}} = 0.456$ eV).

Fig. 3. Comparison of F-Xe $I(\theta)$ derived by CC and elastic methods for $E_{\text{rel}} = 0.456$ eV. Arbitrary scaling is employed. (a) CC result with no angular averaging. (b) Elastic result with no angular averaging. (c) Angular average of curve (a). (d) Angular average of curve (b).

Fig. 4. Comparison of F-Xe $I(\theta)$ derived by CC and elastic methods for $E_{\text{rel}} = 0.915$ eV. (a) CC results angular averaged. Slight jagged quality is due to $1/2^\circ$ spacing. (b) Elastic results angular averaged.

Fig. 5. Absolute ($\text{\AA}^2$) (a) $B_\ell(1/2, 1/2; 1)$, (b) $B_\ell(1/2, 3/2; 1)$, (c) $B_\ell(1/2, 3/2; 2)$ and (d) $B_\ell(3/2, 3/2; 3)$ versus ℓ , the nuclear orbital angular momentum, for F-Xe at the total $E = 0.0414$ eV. Note individual scaling shown.

Fig. 6. Same as in Fig. 5, except for $E = 0.405$ eV, F-Xe.

Fig. 7. The F-Ar interaction potentials. Same notation as Fig. 1.

Fig. 8. Same as in Fig. 4, except for F-Ar at $E_{rel} = 0.108$ eV.

Fig. 9. Same as Fig. 5 except for F-Ar at $E = 0.0582$ eV.

Fig. 10. The Cl-Xe interaction potentials. Same notation as Fig. 1.

Note these potentials are slightly different than the recommended values of Ref. 12, see text.

Fig. 11. Same as in Fig. 3, except for Cl-Xe at $E_{rel} = 0.112$ eV.

Fig. 12. Same as in Fig. 5, except for Cl-Xe at $E = 0.00282$ eV.

Fig. 13. Comparison of the CC computed $I(\theta)$ (solid line) and the experimental results (solid circles) of Ref. 11 for F + Ar at $E_{rel} = 0.108$ eV. Error bars represent ± 1 standard deviation of the mean (90 to 95% confidence limits).

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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Fig. 6

XBL 7811-12993

Fig. 7

Fig. 8

XBL 7812-13199

Fig. 9

XBL 7812-13201

XBL 7811-12992

Fig. 10

XBL 7812-13200

Fig. 11

XBL 7812-13228

Fig. 12

Fig. 13.

XBL 791-7600

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