Nonadiabatic Theory of Fine-Structure Branching Cross Sections for Na-He, Na-Ne, and Na-Ar Optical Collisions

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Nonadiabatic theory of fine-structure branching cross sections for Na-He, Na-Ne, and Na-Ar optical collisions

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The nonadiabatic close-coupled theory of atomic collisions in a radiation field is generalized to include electron spin and is used to consider the weak-field Na—rare-gas (RG) optical collision Na(2P1/2, 3P1/2) + RG + n\hbar\nu → Na(2Pj) + RG + (n - 1)\hbar\nu. The effects of detuning and incident energy on the branching into the atomic Na 3p 2P1/2 and 3p 2P3/2 states are examined. The cross sections \sigma(j) are found to have a strong asymmetry between red and blue detuning as well as a complex threshold and resonance structure dependence on energy. A partial cross-section analysis of \sigma(j) shows a significant difference between contributions from states of e and f molecular parity. The theoretically calculated detuning dependence of the branching ratio into each fine-structure state is in good agreement with available experimental data for Na-Ar, Na-Ne, and Na-He, as well as the total absorption coefficient for the production of Na 3p atoms. The fine-structure branching ratio for thermal energy collisions shows considerable variation with a rare-gas collision partner, due to the different interaction potentials. For sufficiently high collision energy, the branching approaches a recoil limit which is independent of collision partner.

I. INTRODUCTION

For some time, there has been considerable interest in studying nonadiabatic effects in atomic and molecular collisions. These effects play an essential role in determining final-state distributions in the usual elastic or inelastic scattering between atoms or molecules. More recently, emphasis has been placed on the role of nonadiabatic coupling in determining final-state distributions in photoionization, molecular dissociation, and collisional redistribution of light.1–24 These processes have been broadly termed photofragmentation. The final-state distributions of the photofragments may be conveniently described in terms of the multipoles produced among various final states accessible to the system.

In this paper, we consider spin-orbit effects in far-wing collisional redistribution of light for Na—rare-gas systems. In particular, we compute the total cross section \sigma(j) for production of each fine-structure state of the Na 3p multiplet by optical collisions with He, Ne, and Ar. We find that the cross section \sigma(j) depends strongly on the interatomic potentials, the degree of detuning from resonance, and the scattering energy. Similar calculations have also been carried out by Kulander and Rebentrost for the Na+Ar system.10,11 Our work differs from theirs in that we also calculate the effect of He and Ne perturbers and use a different set of potentials for Na-Ar. We also illustrate how the factorization of the radiative S matrix by a generalized multichannel quantum-defect analysis14 leads to considerable insight into the nature of the absorption profile and fine-structure branching.

Before presenting the nonadiabatic close-coupling theory with spin, we give a broad outline of the physical processes by considering nonadiabaticity from the viewpoint of coupling between states using various Hund’s-case basis sets.25 We follow this by discussing nonadiabatic collision dynamics in terms of a distorted-wave analysis of the radiative scattering matrix.14

A. Nonadiabatic collision dynamics: Molecular basis sets and nonadiabatic mixing

Consider the absorption of light during a strong collision, followed by fragmentation of the molecule into electronically excited products:

\[ A + RG + n\hbar\nu → A^* + RG + (n - 1)\hbar\nu, \tag{1} \]

where A and RG represent the alkali-metal (Na here) and rare-gas atoms, respectively; n is the number of photons of energy \hbar\nu in the incident laser field. The phonon energy \hbar\nu is chosen so that the only energetically allowed outcome of the collision (1) is to leave RG in its ground state while exciting the Na atom (A*) to its 3p 2P1/2 and 3p 2P3/2 states. The Born-Oppenheimer (BO) potentials for the Na-RG systems are shown schematically in Fig. 1. A single-mode laser field of frequency \nu causes electronic transitions from free \(E > 0\) states of the molecular XΣ ground state to free \(E' > 0\) states of the excited molecu-
lar electronic $A\Pi$ and $B\Sigma$ states. From energy considerations, $E + h\nu = E' + h\nu_0$ with $\Delta$, the detuning from resonant excitation, given by $\Delta = h(\nu - \nu_0)$. With the usual assumptions, the classical Franck-Condon principle tells us that for any particular $\nu$, the electronic transitions occur in the vicinity of the internuclear separation $R^*$ where the difference between the upper and lower potentials equals the excitation frequency $\nu$.27

The BO potentials are just the internuclear-separation $(R)$-dependent eigenvalues of the electronic part $(H^e)$ of the total molecular Hamiltonian $H_\text{mol}$. $H^e$ does not include the spin-orbit $(H^{so})$ or rotational $(H^{rot})$ interactions.28 It is convenient to introduce a Hund's case-(a) molecular basis $\{|JM_p;S\Lambda\Sigma\}$ to represent the electronic-rotational states. Here $J$ and $M$ are the total and space-fixed projection of the molecular angular momentum, $p$ the molecular parity, and $\Lambda(\Sigma)$ the magnitude of the projection of the electronic orbital (spin) angular momentum onto the moving, molecule-fixed internuclear axis.28 $S$ is the spin. In the absence of the radiative coupling $J$, $M$, and $p$ are strictly conserved during a collision. However, the spin-orbit and rotational interaction parts of the molecular Hamiltonian mix states of different $\Lambda$ and $\Sigma$.29 Thus, in the Hund's case-(a) representation, it is these interactions which give rise to nonadiabatic coupling.

Since the case-(a) Hamiltonian is nondiagonal in spin-orbit coupling and, in particular, is asymptotically nondiagonal, it is often convenient to choose as a basis the Hund's case-(c) representation $\{|JM_p;J_\Omega\}$,28,29 where $J_\Omega$ is the atomic electronic angular momentum (which is well defined as $R \to \infty$) and $\Omega$ is the projection of $J_\Omega$ on the internuclear axis. In this basis, the spin-orbit operator $H^{so}$ is diagonal so that the diagonal elements of $H_\text{mol}$ approach the correct fine-structure splitting as $R \to \infty$. In case (c), off-diagonal terms proportional to the BO difference potentials mix states of the same $\Omega$, and rotational coupling terms mix states of different $\Omega$. Thus, the case-(c) Hamiltonian is strongly nondiagonal in the small-$R$ regions where far-wing absorption occurs, since the electronic splitting is much larger than the spin-orbit coupling terms. The case-(c) Hamiltonian is also nondiagonal at large $R$ where rotational coupling terms varying as $R^{-2}$ mix states of different $\Omega$ and of the same $J_\Omega$. As $R \to \infty$, the molecular Hamiltonian is diagonal in the case-(e) representation, $\{|JM_p;J_\Omega,l\}$,28 where $l$ is the quantum number of relative rotational angular momentum for the two atoms, i.e., $J = J_\Omega + l$. The case-(e) states are the channel states of scattering theory,30 and the scattering boundary conditions are applied to the total wave function expanded in the case-(e) basis. The off-diagonal matrix elements in case (e) are proportional to the BO difference potentials and cause strong coupling, at small internuclear separations, of case-(e) states.31

At times, it is convenient to define a basis that is not a pure Hund's case of angular momentum coupling.32 One useful choice is to diagonalize $H^e + H^{so}$ as a function of $R$, neglecting the rotational coupling terms. The resulting states have the property that they go to case (c) asymptotically as $R \to \infty$ and to case (a) at small $R$ where the separation of BO potentials is large compared to the non-diagonal coupling terms. The potentials defined this way provide an adiabatic correlation between the short-range case-(a) states and the long-range case-(c) states. Figure 2 shows these potentials for the Na-Ar system.

Thus, the concept of nonadiabaticity should be discussed in conjunction with the representation of the molecular state. Since the different Hund's bases are connected by unitary transformations, they are formally equivalent for constructing the close-coupled equations. Nevertheless, some representations are more convenient than others in considering the process Eq. (1). For example, for detunings in the far wings of the line profile, the Condon point(s) of stationary phase occur(s) in a region of internuclear separation where the excited-state Hamiltonian matrix is nearly diagonal in the Hund's case-(a) basis. Thus, for far-blue-wing detuning, excitation is to a nearly
pure \( B \Sigma \) state, while for far-red detunings, the excitation is to a predominately \( A \Pi \) state. Under these circumstances, photon absorption is readily understood as \( B \Sigma \leftrightarrow X \Sigma \) or \( A \Pi \leftrightarrow X \Sigma \) molecular transitions.

In case (a), the nonadiabatic dynamics which determine the distribution of final states occur at intermediate internuclear separations where the off-diagonal spin-orbit and rotational terms in the Hamiltonian become comparable to the final-state BO difference potentials. If some representation other than case (a) is used in the \( R \) range where absorption occurs, then the photon excitation must be thought of as producing not a single state in this basis, but a coherent mixture of states which are propagated using a strongly nondiagonal Hamiltonian.

B. Distorted-wave analysis

The full radiative, close-coupled scattering calculations, presented in the following section, directly give the desired reduced radiative transition matrix elements \( S_{fi} \). These are all that are required in order to give the full close-coupled results discussed in this paper. However, a distorted-wave analysis of these matrix elements for weak fields is quite helpful in giving some insight into the molecular dynamics between absorption and detection. The desired matrix elements are\(^{15,21}\)

\[
S_{fi} = -2\pi i(2\pi \hbar \omega \phi /c)^{1/2}(\Psi^- | \hat{\mathbf{e}} : \mathbf{\mu} | \psi^+ ).
\]

One feature of (6) is that the excitation amplitude \( D(f \leftrightarrow X^2 \Sigma_{1/2}) \) is made up of a coherent sum of amplitudes from each of the excited electronic states. Of course, choosing the photon frequency allows us to select either predominant \( \Sigma \) or \( \Pi \) excitation. For far-blue-wing detuning, the antistatic \( d(\Pi \leftrightarrow \Sigma) \) excitation amplitude is negligible compared to the quasistatic \( d(\Sigma \leftrightarrow \Sigma) \) factor, and vice versa for far-red-wing detuning.

One important feature of our postulated conditions (absorption into a region of uncoupled, or adiabatic, molecular states) is the unitarity of \( N^- \).\(^{14}\) Therefore, the \( N^- \) factors in (6) disappear when a summation over final
The total absorption coefficient (or equivalently, the total cross section), while is proportional to the sum in (7), is expressed in terms of the adiabatic Franck-Condon matrix elements (5). This presumes, of course, that absorption occurs at stationary-phase points in a region where suitable adiabatic reference potentials can be defined. This condition is normally satisfied in the line wings. Thus, Eq. (7), based on the factorization (4), shows why the simple semiclassical, or quasiatomic, wing profiles agree so well with the nonadiabatic quantum close-coupled results; the semiclassical approximation to the adiabatic Franck-Condon factors is quite good for isolated Condon points. This favorable quantum-quasistatic comparison of wing absorption has been demonstrated both for O(1S→1D) + Ar (Ref. 8) and for Na(3P₁→3S₁/₂)+Ar.\(^{11}\)

The introduction of the \( N^- \) matrix enables us to devise a time-independent “half-collision” quantum-mechanical analog of the time-dependent, semiclassical picture which has been used for “whole-collision” depolarization cross sections.\(^{26,33}\) In the present case, the initial-state collision prepares the molecule for absorption. The absorption process is described by the quantum transition probability amplitude, and the nonadiabatic dynamics in the final state is described by \( N^- \). The final-state scattering may be viewed as a progression from regions of one Hund’s case to another.\(^{26,33}\) It is possible to set up time-independent coupled equations for \( N^- (R) \) which integrate \( N^- \) from the absorption region, where \( N^- = 1^0 \), through the regions of nonadiabatic coupling to the asymptotic region where scattering boundary conditions can be applied to extract the desired asymptotic \( N^- \) matrix.\(^{14}\) We may thus attempt to obtain either fully quantal solutions, or semiclassical approximations, to the \( N^- \) matrix. Since our present paper concentrates on our full radiative, scattering, close-coupled results, we defer any detailed analysis of \( N^- \) to the future. However, there are simple limiting cases for \( N^- \) which give some insight into the nonadiabatic dynamics.

The simplest approximation to \( N^- \) is an adiabatic correlation. For example, we could define adiabatic potentials that connect the short-range molecular states to the long-range \( 2P \) states by diagonalizing the electronic plus spin-orbit Hamiltonian as a function of \( R \). In an adiabatic correlation, \( N^- \) is diagonal and \( B \Sigma_{1/2} \), \( A \Pi_{3/2} \), and \( A \Pi_{1/2} \) correlate, respectively, with \( 2P_{1/2}, 2P_{3/2}, \) and \( 2P_{1/2} \). This leads to branching (as per Sec. III) ratios of 0 for far-blue detuning and 1 for far-red detuning. Such behavior is not observed in our close-coupled calculations, except under special circumstances, so an adiabatic approximation to \( N^- \) is unsatisfactory for the systems we have examined.

Another simple approximation to \( N^- \) is to use the recoil limit, which is a “sudden” approximation, applicable at large fragment separation velocity. This limit has been extensively studied recently by Singer et al.\(^{20}\) in the context of diatomic photodissociation. There is a close relationship between the theories of laser-assisted collisions and photodissociation.\(^{14,21}\) In fact, expression (3) can be used for photodissociation as well, except that the initial-state dynamical matrix \( \mathbf{M}_+ \) is missing and \( \mathbf{d} \) becomes a set of bound-free adiabatic Franck-Condon amplitudes. From the standpoint of final-state dynamics, photodissociation and laser-assisted collisions are treated the same way, and are described by the same \( \mathbf{M}_- \) matrix. In the recoil limit, the atoms are assumed to separate so rapidly that no angular momentum recoupling occurs before the atoms are well separated. The distribution of asymptotic atomic states is thus obtained simply by projecting the molecular state prepared by optical excitation onto the asymptotic channel states. These coefficients are given by a simple unitary transformation, in our case, the \( (a)\rightarrow(e) \) transformation. Singer et al.\(^{20}\) were able to show for the special case where one of the product atoms is in an \( S \) state that the total fine-structure branching ratios (that is, summed over the \( 2j + 1 \) spatial degeneracy of each \( j \) state) are statistical. Thus, for our problem, the recoil limit predicts a branching ratio of 0.5, irrespective of whether the detuning is to the red or to the blue, and irrespective of collision partner (He, Ne, or Ar).

Finally, the recoil-limit prediction is not altered by strong nonadiabatic mixing (due to, for example, a curve crossing) occurring at a smaller internuclear separation than the case \( (a)\rightarrow(e) \) transformation region. However, the manner by which the recoil limit is approached (either as a function of scattering energy or detuning) will depend on that mixing.

II. CLOSE-COUPLED EQUATIONS

As the details of the quantum-mechanical close-coupled theory of atomic collisions in a radiation field have been described in several recent papers\(^{11,30,34,35}\) we will only present a brief discussion here.

A. Hamiltonian

The Hamiltonian \( H \) is given by

\[
H = H_{\text{mol}} + H_{\text{rad}} + V_{\text{rad}},
\]

where \( H_{\text{rad}} \) is the free photon field Hamiltonian and \( V_{\text{rad}} \) is the dipole interaction operator which couples the molecular and radiative degrees of freedom. The total molecular Hamiltonian, \( H_{\text{mol}} \), in barycentric coordinates is given by

\[
H_{\text{mol}} = H^*(r,R) + B(R)L_R^2 + H^{40} + T,
\]

where \( H^* \) is the electronic Hamiltonian whose eigenvalues are the BO potentials \( W_A(R) \):

\[
H^*(r,R)\Psi_e(r,R) = W_A(R)\Psi_e(r,R).
\]

Here \( r \) represents the electron coordinates and \( R \) is the internuclear separation. \( T \) is the kinetic energy operator (relative to the center of mass) and \( B(R)L_R^2 \) is the rotational operator with \( L_R = J - L - S \) and \( B(R) = \hbar^2/2\mu R^2 \).

\( L \) and \( S \) are the electronic orbital and spin angular momentum operators, while \( J \) is the total angular momen-
B. Wave functions

We introduce a Hund's case-(a) molecular basis augmented by the radiation field

\[ |j\rangle = |JMP;SΛΣ\rangle \otimes |nhν, e_0\rangle, \]

where we consider a single-mode radiation field with \( n \) photons of frequency \( ν \) and a linear polarization vector \( e_0 \) in the \( z \) direction. In this representation, the nonrelativistic electronic Hamiltonian is diagonalized, but both the rotational and spin-orbit Hamiltonians have nonzero off-diagonal terms. The molecular parity is defined with respect to inversion of all particle coordinates so that

\[ |JMP_\pm, SΛΣ\rangle = (2)^{-1/2} \left( |JM;SΛΣ\rangle \pm |JM;S-Λ-Σ\rangle \right) \]

with parity defined by \(^{36}\)

\[ p_- = (-1)^J - 1/2, \quad e \text{ parity} \]
\[ p_+ = (-1)^J + 1/2, \quad f \text{ parity}. \]

C. Close-coupled equations

For each initial total angular momentum \( J \) and parity, we expand the total wave function:\(^{36}\)

\[ \Psi_j(E, R) = \sum_f \langle j | F_{ij}(E, R) + \sum_f \langle j | F_{ff}(E, R) \otimes R. \]

Here \( E \) is the scattering energy, \( |j\rangle \) is the initial state, and the sum over the final states includes all channels that can be reached from the initial state by either radiative or nonradiative transitions. The amplitudes \( F_{ij}(R) \) and \( F_{ff}(R) \) satisfy coupled radial equations:\(^{36}\)
### TABLE II. Reduced e-parity matrix elements of the dipole coupling $V^\text{re}$, evaluated in a Hund's case (a). $J$ is the lower-state angular momentum and the signs in parentheses change the e- to f-parity reduced matrix elements.

| Branch | $\langle B^2\text{I}_{1/2} | d | X^2\text{I}_{1/2} \rangle$ | $\langle A^2\text{I}_{1/2} | d | X^2\text{I}_{1/2} \rangle$ | $\langle A^2\text{I}_{3/2} | d | X^2\text{I}_{3/2} \rangle$ |
|--------|-------------------------------|-------------------------------|-------------------------------|
| $P$    | $\left( \begin{array}{c} 2J - 1 \\ 4J \end{array} \right)^{1/2} \tau_0$ | $(-) \left( \begin{array}{c} 2J - 1 \\ 8J \end{array} \right)^{1/2} \tau_1$ | $\left( \begin{array}{c} (2J - 1)(2J - 3) \\ 8J(2J + 1) \end{array} \right)^{1/2} \tau_1$ |
| $Q$    | 0                             | $(-) \left( \begin{array}{c} 2J - 1 \\ 8J(J + 1) \end{array} \right)^{1/2} \tau_1$ | $\left( \begin{array}{c} (2J - 1)(2J + 3) \\ 8J(J + 1) \end{array} \right)^{1/2} \tau_1$ |
| $R$    | $- \left( \begin{array}{c} 2J + 3 \\ 4(J + 1) \end{array} \right)^{1/2} \tau_0$ | $\left( \begin{array}{c} 2J + 3 \\ 8(J + 1) \end{array} \right)^{1/2} \tau_1$ | $\left( \begin{array}{c} (2J + 3)(2J + 5) \\ 8(J + 1)(2J + 1) \end{array} \right)^{1/2} \tau_1$ |

### TABLE III. Parameters used in analytical representations of the Na-He, Na-Ne, and Na-Ar (a) $X\Sigma$ and $B\Sigma$ and (b) $A\Pi$ Born-Oppenheimer potentials. (c) contains the Na-Ar CERN parameters. In each case, the internuclear separation $R$ is in atomic units and the potential is in cm$^{-1}$ units. The parameter labels on the right in (b) correspond to Na-Ar only.

(a) Na-He | Na-Ne | Na-Ar
----------|--------|--------
$X\Sigma$ | $B\Sigma$ | $X\Sigma$ | $B\Sigma$ | $X\Sigma$ | $B\Sigma$

(b) Na-He | Na-Ne | Na-Ar
----------|--------|--------
$A\Pi$ | $A\Pi$ | $A\Pi$

(c) Na-He | Na-Ne | Na-Ar
----------|--------|--------
$X\Sigma$ | $B\Sigma$ | $A\Pi$

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associated with the presence of nonvanishing asymptotic radiative couplings in optical collisions are described in the Appendix of Ref. 21.

D. Potentials and transition moments

To proceed with the determination of the cross sections, we specify the particular BO potentials and dipole transition moments used in our numerical codes. We use two different fits to the Na-Ar (Ref. 37) numerical potentials, and one for Na-He (Ref. 38) and Na-Ne.39

One particular set of potentials for Na-Ar is obtained by using a European Organization for Nuclear Research (CERN) parameter-fitting routine, MINUET. We specify the generic form

\[
V(R) = X_1 e^{-x_2 R} - \frac{\alpha X_3}{R^6} - \frac{\beta X_4}{R^8} - \frac{X_5}{R^{10}},
\]

(19)

where

\[
\alpha = \frac{1}{1 + \exp[-X_6(R - X_7)]},
\]

\[
\beta = \frac{1}{1 + \exp[-X_8(R - X_9)]},
\]

and fix the \( R^{-6} \) coefficient to give the correct asymptotic representation as \( R \rightarrow \infty \). The particular parameter values so determined are listed in Table III.

An alternate representation of the ground and excited \( \Sigma \) potentials also used had the form

\[
V_2(R) = D_e \left[ 1 - \exp[-a_1(R - R_e)] \right]^2
\]

\[
\times \left[ 1 - a_2 \exp[-(R - a_3)^2/a_4^2] \right] - D_e
\]

(20)

with coefficients \( a_1, a_2, a_3, \) and \( a_4 \) determined by a standard least-squares fit. \( D_e \) is the dissociation energy and \( R_e \) is the equilibrium position. For Na-Ar, we use the numerical potentials of Saxon et al.,37 while for Na-He, we use the theoretical potentials of Pascale,38 and for Na-Ne, the potentials of Peach.39,39 For Na-Ar, the \( 1\Sigma \) BO potential is fitted to a Thakkar potential40

\[
V_1(R) = D_0 \left[ 1 - \left( R_e/R \right)^p \right]
\]

\[
\times \left[ 1 + \sum_{i=2}^6 b_i \left( 1 - R_e/R \right)^i \right] - D_e
\]

(21)

with the dissociation energy

\[
D_e = D_0 \left[ 1 + \sum_{i=2}^6 b_i \right].
\]

The coefficients \( b_i \) and the parameters \( D_0, D_e, \) and \( p \) are obtained by a least-squares fit.

For Na-He and Na-Ne, we use

\[
V_1(R) = D_0 \exp(-C_0 R) - C_6/(10R)^6
\]

\[
- C_8/(10R)^8 - C_{10}/(10R)^{10}.
\]

(23)

The transition dipole moments \( \tau_0 \) and \( \tau_1 \) are taken from the Na-Ar calculations of Laskowski et al.41 The dipole moments are nearly equal and have an approximately constant value of 2.6 a.u. over the range of internuclear separations of interest; they are nearly equal to that of the atomic Na 3s-3p transition (2.52 a.u.). The fine-structure coupling coefficient \( A(R) \) is treated as constant and equal to its atomic Na value of 11.46 cm\(^{-1}\). On the basis of spectroscopic studies, this is an excellent approximation for Na-Ne,42 and we have applied it also to the electronically similar Na-Ar and Na-He molecules. The \( \text{ab initio} \) calculation of Cooper43 of \( A(R) \) for Na-Ar also supports this approximation at distances \( R > 9a_0 \), the range of internuclear separations of interest to us. Spectroscopic results44,45 indicate that \( A(R) \) is not constant (\( -10\% \)) for smaller internuclear separations than those important for the fine-structure transition process of interest here. Numerical values of the parameters used in \( V_2(R) \) and \( V_1(R) \) are summarized in Table III. The BO potentials used are illustrated in Fig. 1.

III. RESULTS AND DISCUSSION

In the numerical computation of the cross sections \( \sigma(j) \), it is convenient to calculate the \( P_-, Q_-, \) and \( R \)-branch partial cross sections for each contributing lower-state angular momentum \( J \) and parity \( p \). Most of the computations were done at a single scattering energy of 200 cm\(^{-1}\) and for a detuning range extending from 500 cm\(^{-1}\) blue to 150 cm\(^{-1}\) red of the center of gravity of the Na 3p multiplet. The scattering energy of 200 cm\(^{-1}\) corresponds closely to \( kT \), with \( T \) the temperature in recent measurements6,46 of fine-structure branching ratios on the systems considered here. The intensity of the incident radiation field was taken to be 1 kW/cm\(^2\). This is a weak field for far-wing excitation and numerically we found that the cross section depended linearly on the incident laser intensity. In all runs, convergence in \( J \) was easily achieved, allowing truncation of the infinite \( J \) series occurring in \( \sigma(j) \).

Our most extensive results are for Na-Ar, and we present those first. In particular, we have also calculated the energy dependence of \( \sigma(j) \) for a blue detuning of 100 cm\(^{-1}\) with energy \( E \) ranging from threshold to 2000 cm\(^{-1}\), allowing us to study the energy-dependent approach to the recoil limit47 discussed in Sec. 1B. We then present our results for Na-Ne and Na-He and compare them to those of Na-Ar. In order to facilitate comparisons with experimental data, it will be convenient to present our results as a normalized absorption coefficient

\[
K(j) = \sigma(j) \nu/\phi
\]

or as a branching ratio

\[
B(\Delta) = K(j = 1/2)/K(j = 3/2).
\]

Here \( \nu \) is the initial relative scattering velocity and \( \phi \) is the photon flux. Note that if \( \alpha \) denotes the Beer's law absorption coefficient then \( K \) is simply the normalized absorption coefficient \( \alpha/[\text{Na}][\text{RG}] \); \( [X] \) represents the density of species \( X \). Note also that in this report detunings \( \Delta \) are measured relative to the center of gravity of the Na 3p multiplet.

A. Na-Ar results

1. \( J \) dependence

Typically, the partial cross sections \( \sigma_j(j) \) display an oscillatory dependence on \( J \), as shown in Fig. 3. These oscillations, which arise through the \( J \) dependence of the excitation amplitudes, depend on detuning and collision en-
energy. It should be noted that a shape or Feshbach-type resonance in \( \sigma_f(j) \) can occur at certain collision energies. At these resonances, the entire cross section can be dominated by the contribution from a single \( J \). We discuss resonances in a later section.

The cutoff in \( \sigma_f \) around \( J_m = 79.5 \frac{\hbar}{\epsilon} \) has an elementary semiclassical explanation. Indeed, for a particular detuning, there is typically a narrow range of internuclear separations, centered at \( R^* \), over which optical transitions take place. For collision energy \( E \), velocity \( v \), and reduced mass \( \mu \), this limits the maximum impact parameter such that \( J_m = \mu v R^*/\hbar \). This estimate of \( J_m \) quite accurately predicts the numerically determined cutoff \( J_m \) in the cross sections for all three Na-RG systems considered here.

2. Parity dependence

The total cross section \( \sigma_f(j) \) can be calculated from the sum of partial cross sections for each branch and initial parity. We find that for each branch \( (P, Q, R) \) the partial cross section depends strongly on parity, Fig. 4. The quantity \( \delta \) (parity) is defined as the difference divided by the sum. The origin of this parity dependence can be seen from Tables I and II which exhibit large parity-dependent diagonal and off-diagonal terms in the case-(a) Hamiltonian. Thus, both excitation \( (V^{\text{rad}}) \) and propagation \( (H^{\text{mol}}) \) contribute to the parity dependence of \( \sigma_f(j) \). An examination of the table reveals that the \( ^2 \Pi_{3/2}^{-2} \Sigma_{1/2} \) coupling matrix element at the curve crossing is different for each parity:

\[
(2)^{1/2}B \left\{ 1 \mp \left[ (J(J+1) + \frac{1}{4}) \right]^{1/2} \right\} + (2)^{-1/2}A ,
\]

with upper (lower) sign for the \( e \) (f) parity. \( A \) is the spin-orbit coupling parameter. If these matrix elements are used in a Landau-Zener model for the curve crossing near \( 12.2a_0 \) in the BO potentials for Na-Ar (Fig. 1), we see that the diabatic transition probability increases with \( J \) for \( f \) parity, but decreases for \( e \) parity. The \( J \) dependence of the \( e-f \) parity differences in \( \sigma_f(j) \) obtained from this model is in general qualitative agreement with the numerical close-coupling calculations. The \( A^{-1} \Pi_{3/2} - A^{-1} \Pi_{1/2} \) rotational coupling is not parity dependent.

3. Energy dependence \( E \) and the recoil limit

The energy dependence of \( K(j) \) is presented in Fig. 5 for a blue detuning of 100 cm\(^{-1}\). The total \( K(1/2) + K(3/2) \) is constant at high \( E \) in accordance with the predictions of the quasistatic theory.\(^{11,27} \) The cross section itself decreases with increasing \( E \) since it is proportional to \( 1/v \).\(^{11} \) Physically, this decrease can be considered to be due to a decrease in the average collision time, with a corresponding decrease in the probability of photon absorption during the collision.

The \( K(j) \) for blue detuning vary smoothly with \( E \). There is some resonance structure (not shown) at very small \( E \) associated with resonances (quasibound levels) in the shallow \( \chi \Sigma \) and \( B \Sigma \) potentials. However, \( K(j) \) for red detuning (not shown) exhibits a considerable amount of complex structure at low \( E \) due to the increased importance of quasibound levels for the deeper \( \Delta \Pi \) potentials. Figure 6 illustrates how a single resonance for \( J = 49.5 \hbar \) is principally responsible for a strong narrow resonance feature near \( E = 71.975 \) cm\(^{-1}\) for a red detuning of 50
cm$^{-1}$. The presence of other (relatively weaker) resonance contributions to the sum is also evident in Fig. 6. In general, the resonance structure is very complex and our computations are on too coarse a grid to map these features accurately. Some resonances are several cm$^{-1}$ in width while others are very narrow ($<0.01$ cm$^{-1}$). The total cross sections can vary by orders of magnitude, making a detailed survey extremely difficult. An estimate of the contribution of quasibound resonances to the thermally averaged spectrum shows that their overall influence is relatively minor in the present case due to the limited phase space available to the resonances.\textsuperscript{49}

The resonances are in some instances $A^2\Pi_{1/2}$ shape resonances, while in others they are $A^2\Pi_{3/2}$ resonances predissociating to the $A^2\Pi_{1/2}$ state. An interesting feature of the resonances is their propensity to decay almost entirely to the asymptotic $2P_{1/2}$ state even when the total energy is above the $2P_{3/2}$ asymptote. As the near-threshold excess energy is virtually all potential (rotational), resulting in slow radial dissociation, this behavior is likely due to adiabatic adjustment of the motion to the $A^2\Pi_{1/2}$ state, with a corresponding adiabatic correlation to the $2P_{1/2}$ state.

At sufficiently high separation velocities, the recoil limit\textsuperscript{20} should predict the fine-structure branching ratio. In this limit, the branching ratio, $K(1/2)/K(3/2)$, for our case will be 0.5, irrespective of collision partner. We expect this to occur when the separation time $\Delta R/v$ is much shorter than a characteristic time of spin-orbit coupling, say $\hbar/\Delta E$. Here $\Delta R$ is some characteristic separation distance from the case-(a) absorption region to the separated atoms and we take $\Delta E$ to be the asymptotic atomic Na $^2P_{3/2}-^2P_{1/2}$ energy difference. If we apply the criterion $v \gg \Delta E \Delta R/v$ and use $\Delta R = 7a_0$, we require the relative separation velocity $v \gg 1.2 \times 10^4$ cm s$^{-1}$. Thus the final-state collision kinetic energy must be much greater than 800 cm$^{-1}$ for Na-Ar and much greater than 200 cm$^{-1}$ for Na-He. Since the final-state total energy $E' = E + \Delta$, the recoil limit may be approached for red- or blue-wing detunings by increasing the initial-state scattering energy $E$. In Fig. 7 we show the energy dependence of the Na-Ar branching ratio $B(\Delta)$ for a blue detuning of $\Delta = 100$ cm$^{-1}$. As discussed in previous paragraphs, while there is considerable low-energy variation in $B(\Delta)$, the branching ratio indeed approaches the recoil limit of 0.5 for large $E$. A similar approach to the recoil limit, with increasing energy $E'$, is found for far-red-wing detuning. In this case the ratio $B$ is less than 0.5 for low $E'$ and increases to 0.5 as $E'$ increases.

An informative test of the effects of the mass of the collision partners is to calculate the energy dependence of $B(\Delta)$ for $\Delta = 100$ cm$^{-1}$ using the potentials for Na-Ar, but the reduced mass of Na-He. These results are also shown in Fig. 7 where we see that in fact the recoil limit is approached for much lower velocity and the departures from the recoil limit are smaller than for the normal calculation with the Na-Ar reduced mass. The same effect is found for red detuning. Note that this result is consistent with the photodissociation calculation of Singer et al.\textsuperscript{18} for Na-H. Although the Na-H potentials are much different than those for the Na-RG molecules, they found that the recoil limit for the Na $^2P$ branching ratio was reached for about 200 cm$^{-1}$ of separation kinetic energy.

The model calculations with Na-Ar potentials and Na-He mass do, for $\Delta = 100$ cm$^{-1}$, show small departures from the recoil limit at high velocity. It is apparent from examining the transition amplitudes [see Eq. (6)] that significant $\Sigma-\Pi$ interference is occurring at $\Delta = 100$ cm$^{-1}$ between the quasistatic $\Sigma$-wing and the antistatic $\Pi$-wing excitation amplitudes. In fact, for this detuning and for 2000 cm$^{-1}$ of recoil kinetic energy, there is only about a factor of 5 difference between the $\Sigma$ and $\Pi$ excitation amplitudes (a factor of 25 in $\Sigma-\Pi$ absorption coefficients). For a larger detuning of $\Delta = 300$ cm$^{-1}$ the interference was greatly decreased and the recoil limit approached more closely.

![Fig. 6. Na-Ar partial cross section $\sigma_{j,j+1/2}$ for the $E=71.975$ cm$^{-1}$ resonance at $\Delta = -50$ cm$^{-1}$. Note that the resonance at $J=49.5\hbar$ is one unit of $J$ wide and about $10^4$ stronger than the resonance at $J=45.5\hbar$.](image)

![Fig. 7. Approach of branching ratio $B(\Delta)$ to the recoil limit for $\Delta = +100$ cm$^{-1}$. Na-Ar and Na-Ar with Na-He reduced mass.](image)
4. Branching ratios and total cross sections

The normalized absorption coefficient\(^8\) \(K(j)\) for Na-Ar as a function of detuning (at energy \(E=200\ \text{cm}^{-1}\)) is shown in Fig. 8. The substantial difference between \(K(1/2)\) and \(K(3/2)\) as a function of \(\Delta\) and the strong red-blue asymmetry in these differences are indicative of the nonadiabatic mixing in the excited states. The asymmetry may be brought out more clearly, and more readily compared to experiment, by calculating a branching ratio \(B(\Delta) = K(1/2)/K(3/2)\). This is shown in Fig. 9 for \(E=200\ \text{cm}^{-1}\). The ratio is a direct measure of the relative population produced in the Na \(^2P_{1/2}\) and \(^2P_{3/2}\) states. For now we note that in an adiabatic limit \(B(\Delta) = 0\) for far-blue detuning \((\Delta > 0)\), when excitation is to the \(B^2\Sigma\) state, while \(B(\Delta) \approx 1\) for red detuning \((\Delta < 0)\). In the recoil limit \(B(\Delta) = 0.5\) for either detuning. In Sec. III C we discuss, through comparisons of our results for Na-Ar, Na-Ne, and Na-He optical collisions, the sensitive dependence of the branching ratios on the interatomic potentials.

In Fig. 9, we compare the branching ratio \(B(\Delta)\), at \(E=200\ \text{cm}^{-1}\), with recent experimental data.\(^{15,46}\) The overall agreement is quite good, particularly considering the energy dependence of \(\sigma(1/2)\) and \(\sigma(3/2)\). We also present in Fig. 9 for \(\Delta = 100\ \text{cm}^{-1}\) a thermally averaged branching ratio which is in good agreement with the experiment. The recent Na-Ar theoretical calculations of Kulander et al.,\(^{11}\) done at a scattering energy \(E=219.47\ \text{cm}^{-1}\), are also presented in the figure. These authors also used a fully quantum-mechanical approach, but numerically solved the the full \(10 \times 10\) set of differential equations. They used the Na-Ar potentials of Duren et al.,\(^{30}\) which are similar, in the asymptotic region, to those used in our calculations. The good correspondence between their calculations of \(B(\Delta)\) and ours is evident from the figure. The difference may be attributed to the strong energy dependence of \(B(\Delta)\) (see Fig. 7) and to the different potentials used in the two calculations.

While the size of the branching ratio \(B(\Delta)\) is principally sensitive to the shape of the BO \(A\Pi - B\Sigma\) difference potentials, the total normalized absorption \(K(1/2) + K(3/2)\) is sensitive to \(X\Sigma - A\Pi\) and \(X\Sigma - B\Sigma\) difference potentials. In Fig. 8, we also compare the total (quantum-mechanical) calculated normalized absorption profile to the experimental one of Jongerius,\(^{31}\) which is consistent with other experimental determinations.\(^{52,53}\) The good agreement with our results is evident, and attests to the quality of the potentials used in our calculations.

B. Na-He and Na-Ne results

1. \(J\) dependence

The partial cross sections for Na-He and Na-Ne also exhibit oscillatory dependence on \(J\), but due to the reduced-mass dependence of \(J_m\), we find

\[
J_m(\text{Na-He}) < J_m(\text{Na-Ne}) < J_m(\text{Na-Ar})
\]

2. Parity dependence

The parity dependence of the partial cross sections for Na-He and Na-Ne is similar to that for Na-Ar, as shown in Fig. 10.

3. Cross sections and branching ratios

Here we see a strong red-blue asymmetry, but in a sense opposite to that for Na-Ar. Here for the blue wing \(K(3/2) > K(1/2)\) while generally \(K(1/2) \sim K(3/2)\) on the red wing. Those differences are clearly brought out in the branching ratios \(B(\Delta)\) for Na-He and Na-Ne optical collisions; these are presented in Fig. 11 for a single scattering energy \(E=200\ \text{cm}^{-1}\) and compared to recent experimental data.\(^{46}\) As discussed in the following section the difference between the Na-Ar case and that of Na-He and Na-Ne is likely due to the considerably greater attraction of the Na-Ar \(B\Sigma\) potential.

FIG. 8. Na-Ar normalized absorption coefficients for production of Na\(^3p\) atoms vs detuning: \(K(1/2)\) and \(K(3/2)\), \(K(1/2) + K(3/2)\). \(E=200\ \text{cm}^{-1}\).

FIG. 9. Detuning dependence of the branching ratio \(B(\Delta)\) for Na-Ar. \(E=200\ \text{cm}^{-1}\). Our calculations (●); calculations of Ref. 11 (○); experimental data of Refs. 15 and 46 (+). Thermal average of our calculations for \(\Delta = 100\ \text{cm}^{-1}\) (★).
C. Discussion

In this section we discuss the general detuning dependence of the branching ratio $B(\Delta)$ and contrast its behavior for the Na-He, Na-Ne, and Na-Ar molecules. The qualitative features of $B(\Delta)$ may be understood as follows. For detunings far into the blue wing final-state scattering energy is increasing with $\Delta$. Excitation is to a predominately $B\Sigma$ state with the contribution from the antistatic $A\Pi$ state wing decreasing rapidly with $\Delta$. The situation approximates the recoil limit discussed previously, and we expect $B(\Delta)$ to approach 0.5 in the far blue wing, irrespective of collision partner. In the near blue wings the $\Sigma-\Pi$ spin-orbit coupling becomes important, as do the detailed shapes of the $A\Pi$ and $B\Sigma$ potentials (Fig. 1). For Na-Ar, the relatively strong attraction in the $B\Sigma$ state ($>A$) produces a reversal of $B(\Delta)$ from expectations based on adiabatic correlation to the atomic Na $3\rho$ states (Fig. 2). The projection of the Na-Ar roots of the diagonalized electronic-rotational Hamiltonian (Fig. 12) onto the case-(a) basis in the vicinity of the curve crossing clearly displays the strong $B^2\Sigma_{1/2}^-\rightarrow A^2\Pi_{1/2}$ diabatic transition that produces the reversal. $B(\Delta)$ thus approaches the recoil limit, with increasing $\Delta$, from above 0.5. For Na-He and Na-Ne, on the other hand, the $B\Sigma$ state attraction is weak ($<A$), resulting in considerably less likelihood of a diabatic $B^2\Sigma_{1/2}^-\rightarrow A^2\Pi_{1/2}$ transition compared to the Na-Ar case. The smaller diabatic transition probability is reflected in the approach (with increasing $\Delta$) of $B(\Delta)$ to the recoil limit from below 0.5 for Na-He and Na-Ne.

In the vicinity of the impact region (within a few cm$^{-1}$) of the atomic Na $^2S_{1/2}$,$^2P_{3/2}$ state, resonant excitation dominates wing excitation of the $^2P_{1/2}$ state, and $B(\Delta)$ becomes small for each Na-RG case. In contrast, within the impact region of the Na $^2S_{1/2}$,$^2P_{1/2}$ transitions $B(\Delta)$ becomes large, due to direct excitation of the $^2P_{1/2}$ state. However, the effect of inelastic collisions is not negligible even in the impact region and they produce finite $B(\Delta)$ even for resonant excitation. The details of our studies of

![FIG. 10. Contributions to Na-He and Na-Ne $K(j=1/2)$ from states of $e$ and $f$ parity as a function of detuning $\Delta$. $E=200$ cm$^{-1}$.](image)

![FIG. 11. Branching ratio $B(\Delta)$ vs $\Delta$ for Na-He and Na-Ne at $E=200$ cm$^{-1}$. Our calculations (●); Na-He experimental data of Ref. 46 (+).](image)

![FIG. 12. Projection of the Na-Ar roots of the diagonalized electronic-rotational matrix onto a Hund's case-(a) basis as a function of internuclear separation. The detuning is 100 cm$^{-1}$, $E=200$ cm$^{-1}$, and the data are for the $P$ branch. $B^2\Sigma_{1/2}$ (▲); $A^2\Pi_{1/2}$ (●). The curves through the data are to guide the eye.](image)
the region between the D lines and in the line cores will be presented in a future report.

In the red wings excitation is principally to the A II state. The $A^2\Pi_{1/2}$ component of this state correlates adiabatically to the $2P_{1/2}$ state, while the $A^2\Pi_{3/2}$ component correlates to the $2P_{3/2}$ state. The $A^2\Pi_{1/2}$ state is coupled only weakly by rotation to the $A^2\Pi_{3/2}$ state. In contrast to the blue-wing results we then have small branching ratios where the $A^2\Pi_{1/2} - B^2\Sigma_{1/2}$ coupling is strong (as in Na-Ar) and larger branching ratios where it is weak (as in Na-He and Na-Ne). Further into the red wings $B(\Delta)$ varies rapidly as a result of scattering resonances in the A II state. Near threshold the Na $2P_{3/2}$ channel closes for a scattering energy 17.196 cm$^{-1}$ higher than for the Na $2P_{1/2}$ channel; this results in a rapid increase in $B(\Delta)$ in this region.

IV. CONCLUSIONS

In conclusion, we have carried out fully quantum-mechanical calculations of fine-structure branching cross sections for Na-He, Na-Ne, and Na-Ar optical collisions. We obtain good agreement with available experimental data$^{15,46}$ and with previous Na-Ar calculations by Kulander et al.$^{10,11}$ The calculations indicate that the recoil limit$^{20}$ gives correct branching ratios for sufficiently high separation velocity and that, even for molecules with identical BO potentials, the approach to the recoil limit is mass dependent. Low-velocity collisions show large departures from the simple recoil limit and from an adiabatic limit. These are a consequence of the detailed nonadiabatic dynamics and are a measure of the influence of the interatomic potentials and nonadiabatic couplings.

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