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Broadening of the Sodium *D* Lines by Atomic Hydrogen. An Analysis in Terms of the NaH Molecular Potentials

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The interatomic forces between sodium and hydrogen atoms which are responsible for the broadening of the sodium *D* lines are discussed in terms of calculated interatomic potential curves for the NaH molecule. The importance of including overlap interactions and of considering both upper and lower states of the transitions is emphasized. A calculation of the line broadening using a molecular model for the pair of colliding atoms with the correct adiabatic limits yields damping parameters of 8.3×10^{-9} rad sec^{-1} with an estimated accuracy of 5–10% under the conditions of the solar photosphere and fits well with the observed wings of the absorption line profiles. The temperature dependence of the broadening is found to be approximately $T^{0.42}$, and the width/shift ratios are of the order of 30:1 for both resonance lines. Cross sections for transitions induced between the fine-structure states $^2P_{3/2}$ and $^2P_{1/2}$ are estimated, and the value $\sigma_{1/2\rightarrow3/2}=(70\pm10)\pi a_0{}^2$ at a velocity of 1.28×10^6 cm sec^{-1} is in agreement with previous calculations. Ground-state spin-exchange cross sections are estimated for hydrogen-sodium collisions as $22\pi a_0^2$ in the same velocity range.

I. INTRODUCTION

The broadening of spectral lines due to collisions with neutral perturbers is usually related to potentials expressed in the form of an inverse power series in the interatomic distance R.[1,2] Such an approach is convenient when the cross section for broadening collisions is much greater than the extent of the excited-state wave functions, and the leading term in the interaction series is sufficient. The cross section is essentially determined by the largest value b_0 of the impact parameter b at which the phase shift is unity. Since the phase shift can be expressed approximately as $\phi=\overline{V}\tau$, where $\overline{V}$ is the average energy of interaction during the collision and $\tau=b/v$ is the duration of the collision, we see that the faster the collision, the greater is the energy of interaction required at b_0 and the more important is the range of interatomic separations at which several terms in the series expansion are necessary and at which overlap contributions are important.

In many cases a single term in the power series has been used to discuss experimental results, but the inadequacy of such a treatment and the importance of repulsive contributions even at laboratory temperatures has been emphasized by several authors.[3-5] Inclusion of repulsion in the form of a Lennard-Jones potential of the 6-12 type was investigated by Hindmarsh, Petford, and Smith,[6] but such an analysis does not give the correct temperature dependence and shift/width ratios in cases where repulsive and attractive forces are approximately of equal importance.[7-9] Also, the usual approximation of a single set of parameters to describe the interatomic potential for all relative orientations of the colliding atoms is clearly invalid for all but S states, since the real situation involves many angle-dependent terms and the variation of the coupling of the spin and orbital angular momenta with interatomic separation. The Lennard-Jones potential can therefore be best considered as a convenient parametrization in the absence of more realistic potentials.

The inclusion of repulsive forces is important for the analysis of the broadening of strong absorption lines in the solar spectrum. It is well known that the wing regions of these lines are determined by the conditions of the photosphere (~5000 °K) and cannot be predicted using elemental abundances derived from equivalent width analysis of weak lines. Particular cases are discussed by O'Mara,[10] by Lambert and Warner,[11] by Chamereaux,[12] and by Muller, Bascheck, and Holweger.[13] In the present paper we are concerned with the particular case of the sodium *D* lines for which the dominant broadening mechanism is collisions with hydrogen atoms, the velocity and density conditions being such as to fall within the region of validity of the impact approximations.

The system Na-H is sufficiently simple to allow reliable calculation of the molecular energies using modern high-speed computers. We have therefore proceeded from such molecular potentials and treated the colliding atoms as a molecule during the collisions. This approach avoids the difficulties of separately computing many terms in the series expansion for the potential in addition to the overlap contributions.

II. MOLECULAR POTENTIAL CURVES

Our scattering analysis, in terms of molecular potential curves rather than in a slowly convergent multipole expansion, requires a detailed knowledge of the molecular eigenfunctions and energies associated with the possible molecular states connecting the $^2S(3s)$ and $^2P_{1/2,3/2}(3p)$ states of sodium and the ground $^2S(1s)$ state of hydrogen. The molecular states arising from the interaction of ground-state sodium and hydrogen are $^1\Sigma^+$ and $^3\Sigma^+$. The states arising from ground-state hydrogen and the excited $^2P_{1/2,3/2}$ state of sodium are $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$, and $^3\Pi$. It is imperative, for the purposes of this study, to choose a procedure for constructing these molecular eigenfunctions that assures proper limiting behavior at the separated atom limits. An analysis of the molecular symmetry type indicates that the lowest $^3\Sigma^+$ and $^3\Pi$ states have molecular orbital (MO) assignments $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(3\sigma)(4\sigma)$ and $(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)(2\pi)$, respectively. These two states are, therefore, correctly representable by Hartree-Fock (HF) wave functions in the limit of large internuclear separations. All other molecular states needed for the scattering analysis either do not have the proper limiting behavior within the HF framework or are not representable at all within this model. These considerations dictate that a more general method of analysis is required to adequately describe the NaH molecular system.

The calculation procedure chosen for these studies is the valence-configuration-interaction (VCI) method.[14,15] A spin-free nonrelativistic electrostatic Hamiltonian is employed within the Born-Oppenheimer approximation. For a diatomic molecule this approximation leads to an electronic Hamiltonian depending parametrically on the internuclear separation R. Electronic wave functions $\psi(R)$ are made to be optimum approximations to solutions of the Schrödinger equation

$$H(R)\,\psi(R)=E(R)\,\psi(R) \tag{1}$$

by invoking the variational principle. The specific form for $\psi(R)$ may be written as

$$\psi(R)=\textstyle\sum_\mu c_\mu \psi_\mu(R)\ , \tag{2}$$

where each $\psi(R)$ is referred to as a configuration and has the general structure

$$\psi(R)=A\mathcal{O}_s\prod_{i=1}^{n}\psi_{\mu i}(\tilde{r}_i,R)\,\theta_{M_s}\ , \tag{3}$$

where $\psi_{\mu i}$ is a spatial orbital, A is the antisymmetrizing operator, $\mathcal{O}_s$ is the spin-projection operator for spin quantum number S, and θ_{M_s} is a product of α and β one-electron spin functions of magnetic quantum number M_s. If no restriction is imposed as to the double occupancy of the spatial orbitals, Eqs. (2) and (3) can describe a completely general wave function.

In HF calculations, $\psi(R)$ is restricted to a single $\psi_\mu(R)$ which is assumed to consist as nearly as possible of doubly occupied orbitals. These orbitals are then selected to be the best linear combination of basis orbitals (LCAO) that satisfy the variational principle. The HF computational method has been thoroughly discussed in the literature.[16,17] In configuration-interaction calculations, the summation in Eq. (2) has more than one term, and the c_μ are determined from the secular equation

$$\textstyle\sum_\mu(H_{\mu\nu}-ES_{\mu\nu})c_\nu=0\ , \tag{4}$$

where

$$H_{\mu\nu}=\int\psi_\mu^*(R)\,H(R)\,\psi_\nu(R)\,d\tau\ ,$$

$$S_{\mu\nu}=\int\psi_\mu^*(R)\,\psi_\nu(R)\,d\tau\ . \tag{5}$$

Equation (4) is solved by matrix diagonalization. The matrix elements $H_{\mu\nu}$ and $S_{\mu\nu}$ appearing in Eq. (4) may finally be reduced by appropriate operator algebra to summations of products of one- and two-electron integrals over the basis functions.

The basis functions chosen for describing the molecular system NaH were optimized Slater-type atomic orbitals (STO's). A minimum basis was chosen for the K and L inner shells of Na and an extended basis was used to describe the valence electrons. Configuration interaction was taken only over the valence-shell electrons (frozen K, L, shell approximation). Such a wave function gives an accurate representation of the interatomic potentials at large internuclear separations but must become poorer at short separations where L-shell polarization effects are important. Both σ- and π-coupled valence configurations were included as well as ionic configurations corresponding to $\mathrm{Na^+H^-}$ and $\mathrm{Na^-H^+}$. The results of these calculations are given in Table I and Fig. 1.

The calculated potential curves for the excited states have been uniformly adjusted by the small calculated error (0.031 eV) in the ^2P-^2S term value in order to ensure proper atomic limiting behavior. An average term value is employed since the Π molecular states are degenerate within our approximate Hamiltonian. To determine the region of validity of the CI wave functions, a parallel HF analysis was carried out for the lowest $^3\Sigma^+$ and $^3\Pi$ states. The HF wave function was optimized as a function of the internuclear separation and thus includes inner-shell distortion and polarization effects. The results of these calculations are also shown in Table I and Fig. 1. They indicate that the region of validity of the potential curves derived from the CI wave functions extends down to about 3 Å, which is adequate for our use.

The most characteristic feature of these calculated potentials is the strong attractive behavior of the first excited $^1\Sigma^+$ state. Examination of the CI expansion for this state indicates that the wave function can be written to a first approximation as

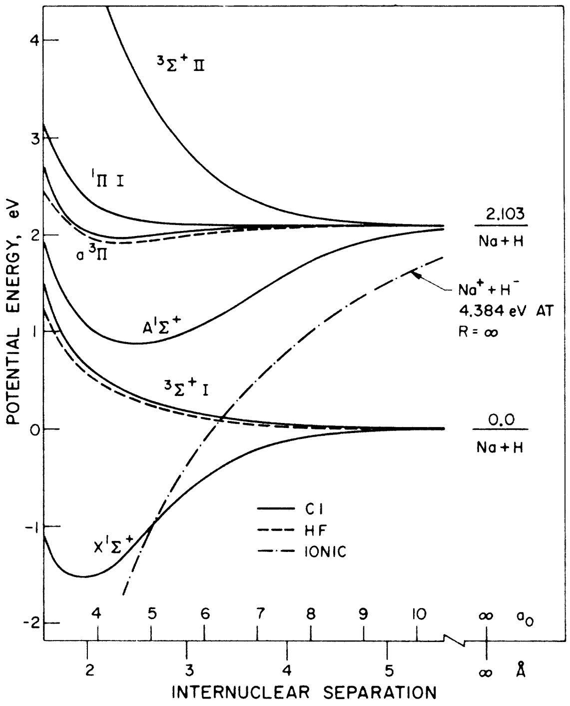

FIG. 1. Sodium hydride molecular potentials.

$$\psi = \psi_{\text{core}}\left[(1s_{\text{H}} + 3p_{\text{Na}})^2 - \lambda\,(1s_{\text{H}} - 3p_{\text{Na}})^2\right] , \qquad (6)$$

where $\lambda \to 1$ for large R and $\lambda < 1$ at shorter separations. Thus the binding is characterized by a doubly occupied σ MO formed from the 1*s* orbital of H and the $3p_0$ orbital of Na. The ground $^1\Sigma^+$ state is similarly characterized by a doubly occupied σ MO formed from 1*s* of H and 3*s* of Na, but here the ionic configuration Na^+H^- appears to have greater weight. The $^3\Sigma^+$ states are characteristically repulsive. The Π states appear to have no strong long-range interaction although the $^3\Pi$ state indicates a slight attraction for shorter separations. These results are all similar to those found by Bender and Davidson[18] in a parallel study of the excited states of LiH.

An important characteristic of these NaH molecular wave functions is common to all of the diatomic alkali hydrides. For all such systems it is necessary to include configurations of an ionic character. In this case the important configuration is Na^+H^- which lies at 4.383 eV above the Na ground state. The variation of the energy of such a configuration with R is essentially a Coulomb curve indicated by the broken line in Fig. 1 and is of $^1\Sigma^+$ symmetry. It is important to note that the $^1\Sigma^+$ ionic state can cause perturbation of the $A\,^1\Sigma^+$ and $X\,^1\Sigma^+$ states at comparatively large internuclear distances. The perturbation of the $X\,^1\Sigma^+$ state is particularly important and at the equilibrium separation it has an ionic character. From the point of the broadening of the *D* lines the ground-state perturbation is significant since the whole of the ground-state perturbation is in the Σ^+ states while the Σ^+ states derived from the resonance levels are statistically only $\frac{1}{3}$ of the interaction in the excited states. It is therefore expected that the ground state will contribute significantly to the broadening of the resonance lines.

The use of these potentials is valid only when the Born-Oppenheimer approximation is valid in its fullest sense. The neglected terms can be thought of as introducing correction to, and mixing between,

TABLE I. Calculated potential energies for NaH. The numbers of configurations for each symmetry type are $^1\Sigma^+$ (12), $^3\Sigma^+$ (8), $^1\Pi$ (8), and $^3\Pi$ (8). The calculated energy at infinite separations for the ground state is − 161.6800 hartree.

R			$^3\Sigma^+$ I				$a\,^3\Pi$	
(bohr)	$X\,^1\Sigma^+$	$A\,^1\Sigma^+$	CI	HF	$^3\Sigma^+$ II	$^1\Pi$ I	CI	HF
∞	0.0	0.077 31	0.0	0.0	0.077 31	0.077 31	0.077 31	0.077 31
15.0	0.0	0.077 31	0.0	...	0.077 31	...	...	...
14.0	0.0	0.077 28	0.0	0.0	0.077 31	0.077 31	0.077 31	0.077 31
13.0	−0.000 01	0.077 26	0.0	...	0.077 30	...	...	...
12.0	−0.000 04	0.077 22	0.000 01	0.0	0.077 30	0.077 31	0.077 31	0.077 35
11.0	−0.000 13	0.076 46	0.000 03	...	0.077 33	...	...	...
10.5	−0.000 22	0.075 88	0.000 05	...	0.077 40	...	...	...
10.0	−0.000 37	0.074 92	0.000 10	−0.000 02	0.077 54	0.077 30	0.077 28	0.077 18
9.5	−0.000 63	0.073 40	0.000 18	...	0.077 81	...	...	...
9.0	−0.001 05	0.071 09	0.000 33	...	0.078 29	...	...	...
8.5	−0.001 75	0.067 77	0.000 57	...	0.079 11	...	...	...
8.0	−0.002 91	0.063 30	0.000 96	0.000 35	0.080 48	0.077 28	0.077 01	0.076 36
7.5	−0.004 77	0.057 77	0.001 56	...	0.082 66	...	...	...
7.0	−0.007 75	0.051 54	0.002 46	0.002 38	0.086 04	0.077 32	0.076 51	0.075 37
6.0	−0.018 77	0.039 73	0.005 48	0.004 05	0.093 66	0.077 59	0.075 35	0.073 85
5.0	−0.037 35	0.033 18	0.010 97	0.009 25	0.124 50	0.078 71	0.073 37	0.071 98
4.0	−0.055 58	0.035 99	0.020 01	0.017 66	0.166 75	0.083 88	0.073 52	0.071 07

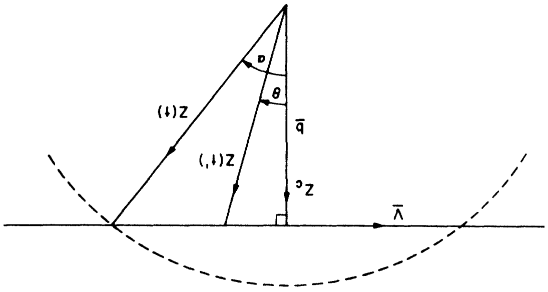

FIG. 2. Collision axes.

the Born-Oppenheimer states ψ_i. Hirschfelder and Meath[19] have discussed these terms which are of the form

$$\frac{1}{2\mu}\sum_k \int \psi_l^* (\vec{r},\vec{R})\, \nabla_R^2 \psi_k (\vec{r},\vec{R})\, d\vec{r}$$

and

$$\frac{1}{2(M_a+M_b)} \sum_{i,k} \int \psi_l^* (\vec{r},\vec{R})\, \vec{\nabla}_i \cdot \vec{\nabla}_j \psi_k (\vec{r},\vec{R})\, d\vec{r} \;,$$

where μ is the reduced mass of the atoms of mass M_a and M_b. A correction is also introduced due to the coupling between the electronic angular momentum and the molecular rotation which leads to Λ doubling in real molecules. Where they have been considered in detail these effects introduce only small corrections to the Born-Oppenheimer energies and are therefore neglected in our treatment.

The present work, therefore, represents an attempt to use realistic molecular potentials in a line broadening calculation for a case in which the use of an expansion in a conventional series in powers of R^{-1} would entail many terms.

III. COLLISION THEORY

At low densities and reasonably high velocities line broadening is determined by two-body collisions of short duration between the excited atom and perturbers. The pressure broadened component of the line shape is then of the Lorentzian form

$$I(\omega) \propto 1/[(\omega_0 - \omega - d)^2 + w^2] \;, \tag{7}$$

where w and d are the real and imaginary parts of the damping parameter

$$\langle N\sigma(v)v\rangle_{\mathrm{av}} = N \int_0^\infty f(v)\, dv\, 2\pi \int_0^\infty b\,[1 - \Pi(b,v)]\, db \;. \tag{8}$$

We work in a product space

$$|j_1,\ m_1;\ j_2,\ m_2\rangle = |N_a,\ j_1 m_1\rangle\, |H,\ j_2 m_2\rangle \;,$$

where only ground-state terms of hydrogen are considered so that the expression for $\Pi(b,v)$ may be written[20]

$$\Pi(b,v) = \sum_{m_i\, m_f, m_k\, m_l, M} (-1)^{2j_i + m_i + m_k} \times \begin{pmatrix} j_f & 1 & j_i \\ m_f & M & -m_l \end{pmatrix} \begin{pmatrix} j_f & 1 & j_i \\ m_l & M & -m_k \end{pmatrix} \times \langle j_i m_i | S_c | j_i m_k\rangle \langle j_f m_l | S_c^{-1} | j_f m_f\rangle \;. \tag{9a}$$

It is understood that a trace over the perturber states weighted by the density matrix has been taken. The S_c denote the scattering matrices for the atomic collision calculated with reference frame defined by the collision for both the initial and final states. The average over the orientation of the collision frames with respect to the laboratory reference frame has been made, for an isotropic environment, in deriving (9). One suitable collision frame defined in Fig. 2 is that for which z_c lies along the impact parameter b. In our calculation we make the approximation, usually referred to as the "classical path," that the perturber with velocity $\vec{v}$ travels along a rectilinear path perpendicular to b.

We denote the sodium ground state $^2S_{1/2}$ as the state f and the excited states $^2P_{1/2,\,3/2}$ as the state i, then since the S matrix for any S state is necessarily diagonal, Eq. (9a) reduces to

$$\Pi(b,v) = \sum_{m_i,\, m_f,\, M} \begin{pmatrix} \frac{1}{2} & 1 & j_i \\ m_f & M & -m_i \end{pmatrix}^2 \times \langle j_i m_i | S_c | j_i m_i\rangle \langle \tfrac{1}{2} m_f | S_c^{-1} | \tfrac{1}{2} m_f\rangle \;, \tag{9b}$$

since all j's and m's are odd half-integers.

To calculate the S matrices we proceed as follows. First we write the coefficients of the atomic functions $|j_1 m_1;\ j_2 m_2\rangle$ as a column vector $|a\rangle$ and proceed in a similar way for the coefficients of the molecular states which describe NaH, then in the notation described

$$|m\rangle = \underline{A}\,|a\rangle \;, \tag{10}$$

where $\underline{A}$ is the matrix for the coupling of the atomic functions into molecular functions.

We have to solve the Schrödinger equation

$$i\hbar \frac{d}{dt}\, |\Phi(t)\rangle = \underline{V}\, |\Phi(t)\rangle \tag{11}$$

and obtain a solution

$$\underline{S}_i = \langle a(t=+\infty) | a(t=-\infty)\rangle \;. \tag{12}$$

The adiabatic solution of (11) is

$$\Phi(t) = \exp\left(-\frac{i}{\hbar}\int_0^t E(t')\, dt'\right)\psi(t) \;, \tag{13}$$

where

$$[\underline{V}(t) - E(t)]\,\psi(t) = 0 \;.$$

Using a molecular basis $|m(t)\rangle\!\rangle$ with internuclear axis as z axis, (11) becomes

$$i\hbar \frac{d}{dt}\, |m(t)\rangle = \underline{V}_z\, |m(t)\rangle \;, \tag{11'}$$

and in the basis $|m'(t)\rangle$ referred to $\vec{b}$ as z axis, we have

$$i\hbar \frac{d}{dt} |m'(t)\rangle = [\underline{D}\,\underline{\tilde{V}}_z\,\underline{D}^{-1} - i\hbar(\underline{\dot{D}}\,\underline{D}^{-1})]|m'(t)\rangle \quad , \qquad (11'')$$

where $\underline{D}$ is the appropriate rotation matrix for the angle θ. Neglecting the second term in square brackets we obtain

$$i\hbar \frac{d}{dt} |m'(t)\rangle = \underline{\tilde{V}}'_{zc} |m'(t)\rangle \ , \qquad (11''')$$

and $\underline{\tilde{V}}'_z$ in Eq. (11′) is always diagonal. Thus the neglect of terms in $\underline{\dot{D}}$ is equivalent to the model in which the pair of atoms is described as a rotating molecule throughout the collision. The approximation is valid if terms of $\underline{\dot{D}}$, which are of the order $\dot{\theta} \simeq v/b \simeq 1/\tau$, are small compared to the interatomic perturbation $\underline{V}$. Clearly for close collisions such a treatment is valid but cannot be used, in general, for the region $b \geq b_0$, where $\underline{V}\tau \leq 1$.

Our derivation of the S matrix is best understood in terms of Fig. 2. If we define an interaction sphere within which the major part of the phase shift occurs and within which the molecular approximation is valid, then (13) becomes

$$|m(+\infty)\rangle = \underline{S}^{(m)} |m(-\infty)\rangle \quad , \qquad (14a)$$

where $\underline{S}^{(m)}$ is the phase-shift matrix

$$S_{ii} = \exp\left(-\frac{i}{\hbar} \int_{-\infty}^{+\infty} V_{ii}(t)\, dt\right) = e^{-i\phi_{ii}} \quad . \qquad (14b)$$

The ϕ_{ii} calculated for a velocity of 10^6 cm $\sec^{-1}$ are plotted against b in Fig. 3. For a collision in which the molecule rotates through 2α we have in the collision frame

$$\underline{S}_c^{(m)} = \underline{D}(\alpha)\, \underline{S}^{(m)}\, \underline{D}(\alpha)^{-1} \qquad (15)$$

and in the atomic basis with respect to the collision frame,

$$\underline{S}_c^{(a)} = \underline{A}^{-1}\, \underline{D}(\alpha)\, \underline{S}^{(m)}\, \underline{D}(\alpha)^{-1}\, \underline{A} \quad . \qquad (16)$$

For close collisions $\alpha \to \frac{1}{2}\pi$ and for distant collisions $\alpha \to 0$, i.e., $\underline{D}(\alpha) = \underline{I}$. These are the two approximations we use for the region $b < b_0$ and $b > b_0$, respectively. While the approximation at large b has, in general, little formal validity, the fact that an average is eventually taken over the m levels of the atomic system leads to close agreement with the results of numerical solutions of (11) in the atomic basis.[21] Clearly, the first term in the expansion of the S matrix, which contributed to the shift, is the same in the rigorous and the approximate treatments which thus give the same limiting behavior at large b.

The form of $\underline{D}(\frac{1}{2}\pi)$ was derived with the assumption that the electron spin and the orbital angular momentum of the sodium atom were decoupled during the collision and that only the orbital angular momentum followed the rotation of the molecular axis. This is justifiable for the excited configuration since the spin-orbit parameters in sodium and magnesium (the united atom limit of NaH) are only 11.5 and 40.5 cm^{-1}, respectively. There is thus not time for the spin to precess about the orbital angular momentum and follow the molecular axis during a close collision. The ground states and the ionic states lead to states of ${}^{1,3}\Sigma^+$ symmetry only for which $\underline{D}(\alpha) \equiv \underline{I}$. In the present case, as will be shown below, the major contribution to the cross sections at large b comes from the lowest ${}^{1,3}\Sigma^+$ states so that the use of (16) with $\underline{D} \equiv \underline{I}$ is a good approximation for $b \gtrsim b_0$.

The molecular basis states used were of the type $|{}^{(2S+1)}\Lambda,\ M_L,\ M_S;\ \Omega\rangle$, rather than the + and − states which are the correct basis for the rotational states of a molecule. The $\underline{A}$ for combinations of ground-state sodium and hydrogen atoms has a simple form, the $|X\,{}^3\Sigma^+, 1, 1; 2\rangle$ and $|X\,{}^3\Sigma^+; -1, -1; -2\rangle$ being identical to atomic products of atomic states and the $|X\,{}^3\Sigma^+, 0, 1, ; 0\rangle$ and $|X\,{}^1\Sigma^+, 0, 0; 0\rangle$ being symmetric and antisymmetric combinations of atomic states. For the states arising from the sodium ${}^2P_{1/2,\,3/2}$ resonance levels and the hydrogen state, the $\underline{A}$ matrix is more complicated, but may be derived simply from the starting point of determinantal product states $|d\rangle$. Since $|j_1 m_1, j_2 m_2\rangle = \underline{P}|d\rangle$ and $|{}^{(2S+1)}\Lambda, M_L, M_S; \Omega\rangle = \underline{Q}|d\rangle$ then $|j_1 m_1, j_2 m_2\rangle = \underline{P}\,\underline{Q}^{-1}|{}^{(2S+1)}\Lambda,\ M_L, M_S;\ \Omega\rangle$. Here we have made the reasonable assumption, justified below, that the spin-orbit interaction in the sodium atom is less than the electrostatic terms for all the interatomic separations R of interest. Thus we proceed directly to Hund's case (b) whereas there is in reality a transition region from case (c) to case (b) at about $14a_0$. In this region the phase shifts are of the order of 0.1 so that neglect of the correct transition between the two coupling conditions will not introduce an appreciable error. The existence of the ${}^1\Sigma^+$ ionic term which strongly perturbs the molecular levels at about $13a_0$ narrows the transition region and reduces the importance of the effect.

The resulting S matrix for the excited state is 12-dimensional, and for the ground state 4-dimensional. Since we are considering the simultaneous effect of a collision on the upper and lower states, and there are no dipole matrix elements between the hydrogen ground states with $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$, we include in our average only terms where the S matrices for the upper and lower levels have simultaneously hydrogen states $m_s = \frac{1}{2}$ or $m_s = -\frac{1}{2}$. The results for the two cases are obviously identical, so that we require only a 6-dimensional excited-state and a 2-dimensional ground-state S matrix.

From Eq. (15) one then obtains, with $\underline{D}(\alpha) = \underline{I}$,

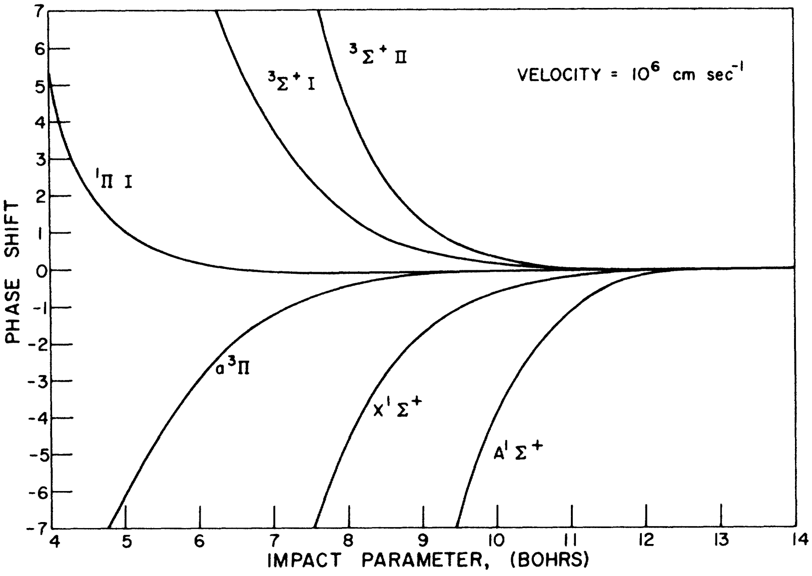

FIG. 3. Phase shifts calculated for relative velocity of collision 10^6 cm sec^{-1}.

$$\Pi_{3/2}(b,v)=\tfrac{1}{36}A\,e^{i\phi(^3\Sigma I)}+\tfrac{1}{36}B\,e^{i\phi(X\,^1\Sigma)}\,, \tag{17a}$$

$$\Pi_{1/2}(b,v)=\tfrac{1}{18}C\,e^{i\phi(^3\Sigma I)}+\tfrac{1}{18}D\,e^{i\phi(X\,^1\Sigma)}\,,$$

$$A=\tfrac{29}{2}e^{-i\phi(^3\Pi)}+\tfrac{7}{2}e^{-i\phi(^1\Pi)}+2e^{-i\phi(^1\Sigma)}+7e^{-i\phi(^3\Sigma)}\,,$$

$$B=\tfrac{7}{2}e^{-i\phi(^3\Pi)}+\tfrac{5}{2}e^{-i\phi(^1\Pi)}+e^{-i\phi(^1\Sigma)}+2e^{-i\phi(^3\Sigma)}\,,$$

$$C=7e^{-i\phi(^3\Pi)}+2e^{-i\phi(^1\Pi)}+\tfrac{5}{4}e^{-i\phi(^1\Sigma)}+\tfrac{13}{4}e^{-i\phi(^3\Sigma)}\,,$$

$$D=2e^{-i\phi(^3\Pi)}+e^{-i\phi(^1\Pi)}+\tfrac{1}{4}e^{-i\phi(^1\Sigma)}+\tfrac{5}{4}e^{-i\phi(^3\Sigma)}\,. \tag{17b}$$

If only the ground-state interactions are important the lines would show equal broadening and shift with

$$\Pi(b,v)=\tfrac{3}{4}e^{i\phi(X\,^3\Sigma)}+\tfrac{1}{4}e^{i\phi(X\,^1\Sigma)}\,, \tag{18}$$

and if only the excited-state interactions are used we again obtain equal shifts and widths for the two lines with

$$\Pi(b,v)=[(2L+1)\,\Sigma_S(2S+1)]^{-1/2}$$

$$\times\sum_{S,M_L}(2S+1)\,e^{-i\phi[^{(2S+1)}|M_L|]}\,. \tag{19}$$

Using the approximation $D(\alpha)=D(\frac{1}{2}\pi)$ and Eq. (16) we obtain the result, valid for small b, in the form of (17a) but with the quantities A, etc., replaced by

$$A'=\tfrac{1}{2}(e^{-i\phi(^3\Pi)}-e^{-i\phi(^1\Pi)}-14\,e^{-i\phi(^3\Sigma)}-4e^{-i\phi(^1\Sigma)})\,,$$

$$B'=\tfrac{1}{2}(-e^{-i\phi(^3\Pi)}+e^{-i\phi(^1\Pi)}-4e^{-i\phi(^3\Sigma)}-2e^{-i\phi(^1\Sigma)})\,,$$

$$C'=\tfrac{1}{24}(7e^{-i\phi(^3\Pi)}-7e^{-i\phi(^1\Pi)}-176e^{-i\phi(^3\Sigma)}$$

$$-42e^{-i\phi(^1\Sigma)})\,,$$

$$D'=\tfrac{1}{24}(-e^{-i\phi(^3\Pi)}+e^{-i\phi(^1\Pi)}-18e^{-i\phi(^3\Sigma)}$$

$$-18e^{-i\phi(^1\Sigma)})\,. \tag{20}$$

In this case the average over perturber states requires the use of the full 12- and 4-dimensional S matrices for the upper and lower states, respectively.

Our formulation also yields an expression for the cross section for transitions between the fine-structure levels $^2P_{1/2}$ and $^2P_{3/2}$ of the sodium atom induced by collisions with atomic hydrogen. This expression is valid when the fine-structure energy separation is neglected and is thus the high-velocity limit. We find that

$$\sigma_{3/2\to1/2}=2\pi\int_0^\infty b\,db\,\tfrac{1}{72}\,[(2e^{-i\phi(^3\Sigma)}$$

$$-e^{-i\phi(^1\Pi)}-e^{-i\phi(^3\Pi)})(\mathrm{c.c})$$

$$+(e^{-i\phi(^3\Sigma)}+e^{-i\phi(^1\Sigma)}-2e^{-i\phi(^3\Pi)})(\mathrm{c.c})$$

$$+3(e^{-i\phi(^3\Sigma)}-e^{-i\phi(^1\Sigma)})(\mathrm{c.c})$$

$$+3(e^{-i\phi(^1\Pi)}-e^{-i\phi(^3\Pi)})(\mathrm{c.c})] \tag{21a}$$

and necessarily obtain

$$\sigma_{1/2\to3/2}=2\sigma_{3/2\to1/2}\,. \tag{21b}$$

From the ground-state collision matrix we find that the cross section for spin exchange between the sodium and hydrogen atoms is

$$\sigma=2\pi\int_0^\infty\tfrac{1}{4}\{1-\cos[\phi(X\,^3\Sigma)-\phi(X\,^1\Sigma)]\}b\,db \tag{22}$$

in the form given by Purcell and Field[22] when hyperfine structure is neglected.

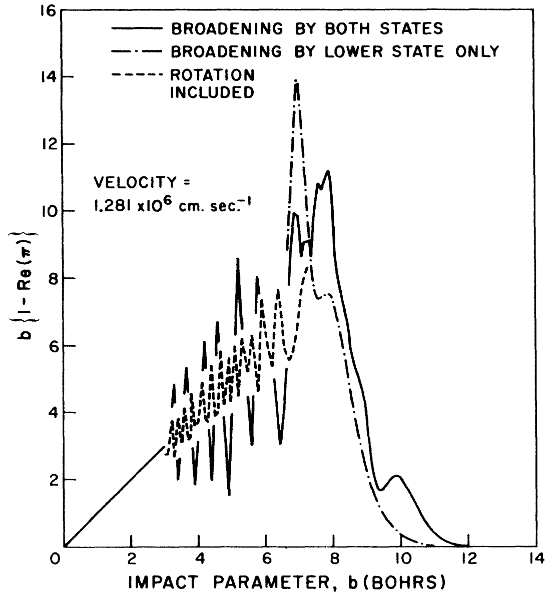

FIG. 4. $P(v, b) = [1 - \mathrm{Re}\Pi(b,v)]b$ for the sodium D_2 line at velocity of 1.28×10^6 cm sec^{-1}.

IV. RESULTS AND DISCUSSION

A. Line Broadening

The S matrices for the upper and lower states were calculated using both (17) and (20) in the velocity range 10^5–10^7 cm sec^{-1} for impact parameters between $3a_0$ and $16a_0$ in steps of $0.1a_0$. Figures 4 and 5 show the behavior of $P(b, v) = [1 - \mathrm{Re}\,\Pi(b,v)]\,b$ and $S(b) = b\,\mathrm{Im}\Pi(b,v)$ for the ${}^2P_{3/2} - {}^2S_{1/2}$ line for velocity 1.28×10^6 cm sec^{-1} which corresponds to approximately the peak of the velocity distribution at the temperature of the photosphere. The corresponding quantities are almost identical for the ${}^2P_{1/2} - {}^2S_{1/2}$ line.

It is interesting to consider the contributions to the cross section from the upper and lower states separately as given by Eqs. (18) and (19). The broken lines in Figs. 4 and 5 are those obtained with the lower state interactions only and clearly give the major contribution to the widths at large b. As discussed above, the rotation of the interatomic axis through the collision does not affect the contribution of these states to the cross section. The small outer peak of $P(b, v)$ is due to the excited ${}^{1,3}\Sigma^+$ states which statistically constitute only $\frac{1}{3}$ of the upper states. When the effects of the upper level alone are considered $P(b, v)$ does not reach its limiting value of $P(b, v) = b$ until $6a_0$, where the ${}^{1,3}\Pi$ states also contribute significantly. The results of the adiabatic theory including rotation give the same limiting behavior at small b as the fixed z axis approximation. In calculating the broadening cross sections, various values of b were taken for the change over in Eq. (16) from $D(\frac{1}{2}\pi)$ to $D(0)$ to estimate the error introduced, which is of the order of 5%. In the region of $8a_0$ neither of these approximations is entirely satisfactory, and the expected uncertainty in our results is discussed at the end of this section.

The shifts obtained are very small and to the red, being about $\frac{1}{30}$ of the full width of the pressure broadened component of the lines. These very small shifts reflect the fact that the levels which mainly contribute to them, the ${}^{1,3}\Sigma^+$ levels, arise in pairs whose centers of gravity are, in the important region of R, displaced very little from the free-atom energy.

The broadening constants calculated with the inclusion of both upper and lower state interactions are essentially equal for the two D lines. The velocity dependence of the broadening and shift cross sections σ_{Re} and σ_{Im} are given in Fig. 6 and, in the region of our calculations, correspond approximately to a variation of $T^{0.42}$ which is intermediate between the van der Waals result of $T^{0.3}$ and the hard-sphere prediction of $T^{0.5}$. Inclusion of only the lower state interactions leads to almost the same exponent for the temperature dependence, but a calculation which includes only the upper state interactions leads to a slightly larger exponent due to the increasing importance of the ${}^{1,3}\Pi$ states with increasing temperature.

Table II summarizes the contributions of the various levels to w and d, after the cross sections have been averaged over a Maxwellian velocity distribution for 5000 °K. We see that the inclusion of

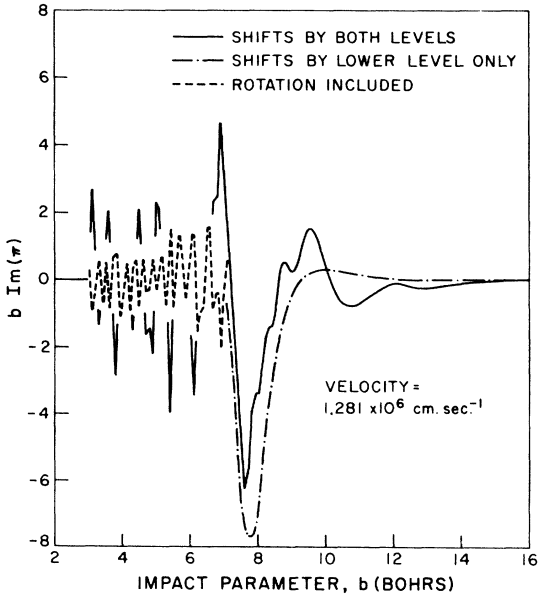

FIG. 5. $Q(b, v) = \mathrm{Im}\Pi(b,v)b$ for the sodium D_2 line at a velocity of 1.28×10^6 cm sec^{-1}.

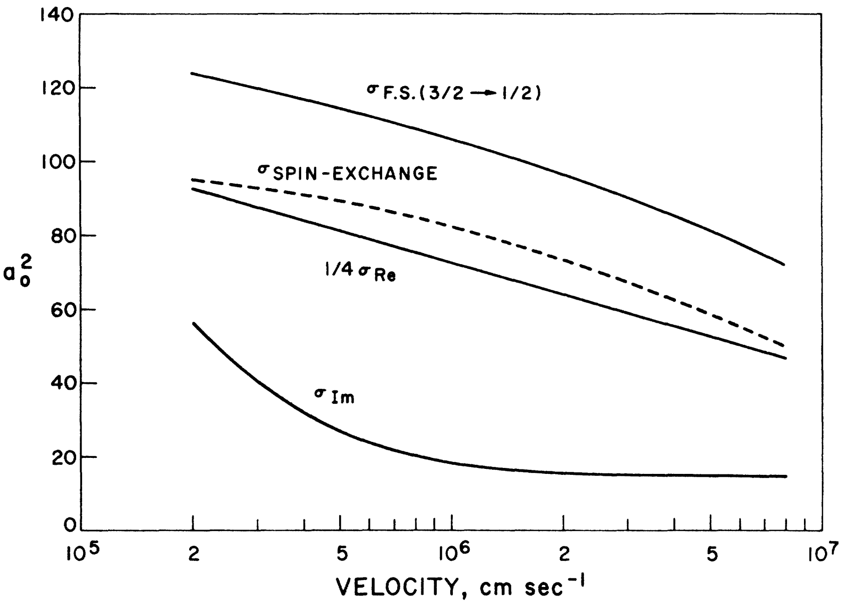

FIG. 6. Temperature dependence of cross sections.

only the lower state leads to widths approximately 10% smaller than the complete result, while the inclusion of only the upper state interactions reduces the widths to $\frac{2}{3}$ of their full value. In all cases the w, d, and width/shift ratio are the same for the two resonance lines. The fine-structure transition rate is included in Table II in the same units as w and d for comparison.

In astrophysical calculations it is usual to work with a single-parameter interaction

$$V(R) = -hC_6 R^{-6},$$

where C_6 is the difference of the quantities $C_6(i) = (e^2/h)\,\alpha\langle r_i^2\rangle$, α is the polarizability of the ground state of the perturber, and $\langle r_i^2\rangle$ is obtained from the approximate expression $\frac{1}{2}\,a_0^2 n^{*2}[5n^{*2}+1-3l(l+1)]$, for the two levels involved in the transition.[23] With these expressions $hC_6 = 90.3$ hartree, where R is in bohrs. With the aid of conventional phase-shift theory[24] one obtains the value given in the fourth line of Table II with a width-to-shift ratio of 2.76 and a temperature dependence of $T^{0.3}$. The result of using our calculated molecular potentials rather than the estimated van der Waals coefficients is to increase the broadening of the resonance lines by a factor of 1.4, which improves the fit to the solar absorption profiles considerably,[25] whereas the existing discrepancy would imply unrealistically an order-of-magnitude error in the C_6 constant.

As yet there are no laboratory measurements of the broadening of the sodium D lines by atomic hydrogen, but such experiments may well be possible in the near future using shock tube techniques. We therefore give the velocity dependence of shifts and widths in full in Fig. 6.

The results of correctly including the rotation of the intermolecular axis at large R have been found to be of the order of 5–10% in the case of resonance broadening[26, 27] in which this region is of importance due to the slowly varying (R^{-3}) nature of the forces. For the reasonance interaction the contribution of collisions with $b > b_0$ is about half the cross section, and for van der Waals (R^{-6}) forces this region contributes only 20% of the cross section so that the effects of neglecting rotation will be only about 2–5%. This has been confirmed by a recent study by Berman and Lamb.[28] For small b we have correctly included the effects of rotation with an error of about 5% introduced by the uncertainty in the transition region. Since the long-range part of the interactions in the present case varies rather faster than R^{-6} we would expect corrections for the rotation at large b to be not greater than 5%. Computational errors are estimated to be less than 2% for the widths and about 10% for the shifts. In drawing Fig. 6 small oscillations of about $5a_0^2$ have been suppressed. Although these are to some extent real, they tend to cancel out in a velocity aver-

TABLE II. Broadening and shift constants for the sodium D lines.

Comment	w/N (10^{-9} rad sec^{-1})	d/N (10^{-9} rad sec^{-1})	$-2w/d$	Fine-structure transition rate ${}^2P_{1/2} \rightarrow {}^2P_{3/2}$
Both levels	8.3	−0.59	28	3.03
Upper level only	6.08	−0.72	17	3.03
Lower level only	7.62	−1.20	12.6	···
van der Waals	5.95	−2.16	2.76	···

age for a given temperature and are therefore not of practical interest. After the velocity average has been performed the width and shift constants should therefore be accurate to about 10% and 20%, respectively.

B. Fine-Structure and Spin-Exchange Transitions

Our result of $63\pi a_0^2$ for the cross section $\sigma_{1/2-3/2}$ at about 10^6 cm sec^{-1} is in good agreement with the result $(70 \pm 20)\ \pi a_0^2$ calculated by Bender *et al.*[29] and should be regarded as a lower limit to the cross section. The velocity dependence of the cross section is given in Fig. 6. As discussed above, the molecular description will have greatest validity at small values of R and should be a good description within the optical broadening cross section.

The question still remains as to whether there is a significant contribution to the cross section from the region $R > 11a_0$. In this region a description of the colliding atoms in terms of an atomic basis set is more appropriate although the magnitude of the interatomic interactions will be indicated by the molecular energies. In the region $R \sim 13a_0$ the interatomic interactions are comparable with the fine-structure splitting of sodium (7.8×10^{-5} a.u.). We may estimate the contribution of this region to the fine-structure transition cross section using the approximate theory of Callaway and Bauer.[30]

If we write the interaction Hamiltonian in the form

$$V_2(R) = U(R)_0 T_0^0 + U(R)_2 T_0^2 \,,$$

where the T_q^k are tensor operators in the product space of the atoms and we neglect the rotation of the system during the collision, we find that only states with $m = \frac{1}{2}$ or $m = -\frac{1}{2}$ are mixed and the probability of a transition resulting from the collision is $\frac{8}{9}\sin^2(0.3\eta)$, where $\eta = (1/\hbar)\int_{-\infty}^{+\infty} U(R)_2 dt$. The upper limit may be estimated by putting $\eta = \phi$, the optical phase shift which has a maximum value 0.2 in the region of interest. The contribution to the cross section from the region $11a_0$ to $15a_0$ is thus at most $5\pi a_0^2$. The inclusion of the rotation of the system during the collision also couples the states $|{}^2P_{3/2}, \pm\frac{1}{2}\rangle$ and $|{}^2P_{3/2}, \pm\frac{3}{2}\rangle$, and this might be expected to double the contribution of this region. Assuming that we may add the effects of the two regions incoherently we suggest a value of $(70 \pm 10) \times \pi a_0^2$ for the cross section $\sigma_{1/2-3/2}$.

From the orders of magnitude discussed above we see that the change in the diagonal elements of the S matrix, which contribute to the line broadening and shifts, will have negligible effect on the line broadening cross section but may well be more important for the shifts.

The ground-state spin-exchange cross section that we have obtained without considering the effects of hyperfine structure is about 20% smaller than the fine-structure transition cross section and the velocity dependence is shown in Fig. 5. The computational error in these values is approximately 5%.

V. SUMMARY

We have shown how the molecular potentials for NaH can be used to calculate line broadening and shift parameters. The contributions of the ground-state perturbations are considerably larger than expected on the basis of van der Waals approximations and contribute significantly to the broadening. In several cases where neutral atom broadening has been observed at high temperatures either in shock tubes[31] or in astrophysical sources[10,13] the broadening has been found to be approximately 50% larger than that calculated using estimated van der Waals constants. Our calculation indicates that this is the size of the correction to be expected when realistic interatomic potentials are used. In the present case observations of the wings of the absorption profiles of the sodium *D* lines from the solar spectrum are in satisfactory agreement with the calculation presented above using our potentials, whereas the van der Waals approximation required an adjustment of the polarizabilities by an order of magnitude. The small red shifts calculated in our approximation are sensitive to distant collisions where our method has less validity so that the shift constants will be less accurate than those for the broadening. Extension of the methods we have used depends on the increasing availability of such calculated molecular potentials and the determination of their long-range limiting behavior from experimental data.

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