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Experimental Potentials for the $X\Sigma+2$ and $A\Pi 2$ States of NaHe

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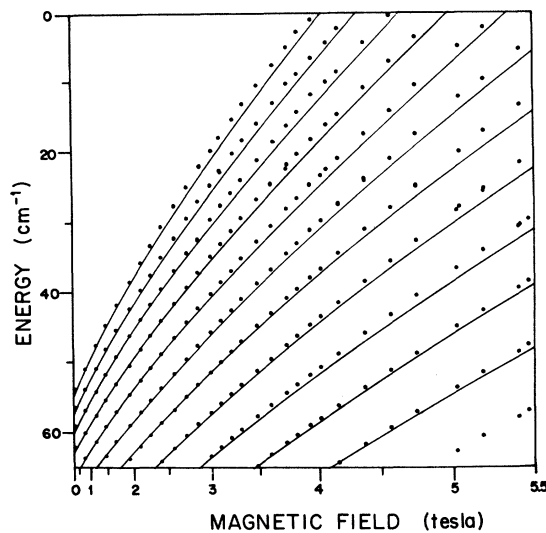


FIG. 4. A comparison of numerical results (solid lines) and experimental results (dots) for the highest level of each manifold for the even-parity, $m_l = -2$ states. The numerical results are obtained by a diagonalization using a spherical basis of Coulombic states, $n = 25-75$ and $l = 2, 4, \text{ and } 6$. The systematic discrepancy, which is less than 1% of the diamagnetic energy, is largely due to the omission of higher- l states.

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Experimental Potentials for the $X^2\Sigma^+$ and $A^2\Pi$ States of NaHe

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Experimental potentials for the $X^2\Sigma^+$ and $A^2\Pi$ states of the NaHe molecule are presented. The potentials are generated from the temperature dependence of the red wing of the Na resonance line perturbed by He. For the $A^2\Pi$ state an unexpectedly large value is obtained for $D_e = 480(50) \text{ cm}^{-1}$ at $R_e = 4.4(2)a_0$. The physical basis for this result, which indicates an important role for the internal structure of the rare gas in determining the repulsive part of the alkali-rare-gas interaction, is discussed.

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In this Letter we report the results of our observations of the temperature dependence of the $A^2\Pi \rightarrow X^2\Sigma^+$ emission spectrum of molecular NaHe. The spectrum, which is observed for 1100 Å on the red side of the He-perturbed Na resonance doublet, is analyzed by using the quasistatic model, as developed by Gallagher and co-workers,¹⁻³ to yield potential curves for the two lowest states of NaHe. For the $A^2\Pi$ state we obtain a remarkably large value for D_e . A deep penetration of the Na $3p\pi$ orbital by the He atom is responsible for this result, which suggests that the internal structure of the rare gas plays an important role in determining the repulsive part

of the alkali-rare-gas interaction.

The interaction of alkali-rare-gas pairs has been studied extensively, with recent work focused on NaNe⁴⁻⁷ and NaHe.^{8,9} The interaction potentials are relevant to interpretation of a variety of elastic and inelastic collision processes involving Na in the $3p$ state. They are also important in evaluation of the suitability of the various alkali-rare-gas combinations for use in a possible rare-gas-metal vapor laser system. Reasonable accord has been reached between model potential calculations^{6,7} and spectroscopic data^{5,10} on the $X^2\Sigma^+$ and $A^2\Pi$ states of NaNe. However, for the NaHe system calculations using

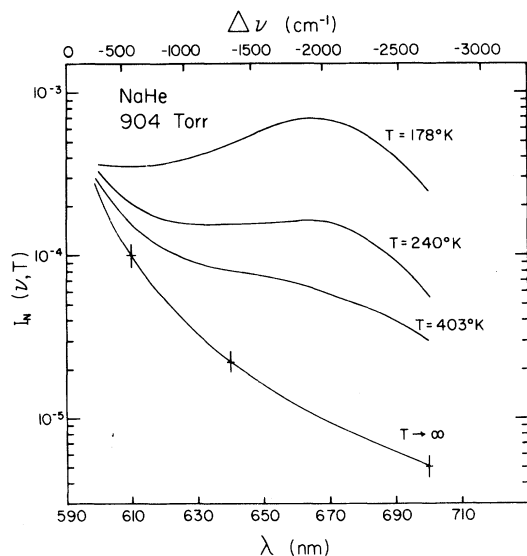


FIG. 1. Normalized red-wing emission spectra for the NaHe molecule, observed with a spectrometer resolution of 32.2 cm^{-1} . On the scale of the ordinate, the resonance line intensity is unity.

a variety of theoretical approaches^{9,11-13} have yielded disparate results. Furthermore, the discrepancy between the far-wing line-broadening experiment of York, Scheps, and Gallagher¹ for NaNe and the results of Ahmad-Bitar, Lapatovich, and Pritchard⁵ has called into question York's results for NaHe.

In our experiment, the temperature dependence of the intensity in the red wing of the Na $3s-3p$ transition perturbed by He was observed in the range 150–330 °K. We go to these relatively low temperatures because, when the excited molecular and atomic populations are equilibrated, a large enhancement of bound molecular to atomic emission results.

Although full details of the experiment will be described in a forthcoming report, a brief description of the apparatus will be given here. The experimental cell consisted of a 250-cm³ Pyrex bulb filled with He gas and mounted with a 6-mm-o.d. sidearm containing Na metal. A styrofoam container was used to insulate the cell from its surroundings. The temperature of the cell was controlled by a flow of cold N₂ gas and measured by a thermocouple attached to the side of the cell. A suitable Na density of 10^{-7} – 10^{-6} Torr was produced in the interaction region by heating the 6-mm-o.d. sidearm with a small resistive heater. In a separate experiment, the temperature determined by a thermocouple in-

serted into the interaction region of the bulb agreed with that of the wall to within our experimental uncertainty of ± 10 °K.

Na atoms were excited to the $3p$ state by a cw dye laser tuned to the D_2 line at 589.0 nm. The approximately 100 mW dye laser output was in a bandwidth of about 0.5 cm^{-1} , well matched to the width of the collision-broadened Na D_2 line. A portion of the resulting atomic and molecular fluorescence was collected and focused onto the slits of a $\frac{1}{2}$ m spectrometer. The spectrometer was mounted with a glass filter which transmitted about 10^{-3} of the Na resonance line and about 90% of all light from 610.0 to 710.0 nm. The filter eliminated spurious signals due to leakage of the intense atomic fluorescence when the spectrometer was tuned to a point on the relatively weak wing profile. The spectral response of the system was calibrated with a 3025 °K tungsten-filament standard lamp.

Normalized emission spectra of the NaHe system are displayed in Fig. 1. The data are reported as

$$I_N(\nu, T) = \frac{2}{3} W n_0 (\nu/\nu_0)^4 |d\nu/dR|^{-1} 4\pi R^2 \times \exp\{[V_u(\infty) - V_u(R)]/kT\}, \quad (1)$$

where the right-hand side is essentially the quasi-static expression² for the red wing in the high-pressure limit. In this limit it is assumed that the atomic and molecular excited state populations are in thermal equilibrium. In the expression for $I_N(\nu, T)$, W is the spectrometer spectral width, n_0 the He gas density, and ν the frequency of the molecular emission. $V_u(R)$ is the depth of the upper-state potential at an internuclear separation $R(\nu)$ and T is the cell temperature. The error bars on these spectra are representative of our estimated maximum uncertainty in normalization and in temperature.

Systematic tests were made for possible variations in $I_N(\nu, T)$ due to laser intensity, Na density, or He gas density. Order-of-magnitude variations of the Na density and laser power produced no measurable effect on $I_N(\nu, T)$. Although the dye laser output was linearly polarized, the atomic and molecular fluorescence we observed was at least 99% unpolarized. To test for possible departures from an equilibrated atomic and molecular excited state population, bulbs were filled with room temperature He pressures in the range 330–2000 Torr. Our results were insensitive, at all bulb temperatures, to the pressure for bulbs containing more than 900 Torr. For

bulbs containing less than 900 Torr He, we observed, at temperatures below 280 °K, departures from equilibrated atomic and molecular populations. The details of our observations will be presented in a future report.

The procedure for generation of potential curves through Eq. (1) and temperature-dependent data such as that in Fig. 1 has been described² in detail in the literature and will not be reproduced here. It has been suggested⁵ that these semiclassical models [including Eq. (1)] may be inadequate to interpret far-wing spectra for the lighter alkali-rare-gas pairs. However, a fully quantal calculation by Herman and Sando⁸ of the bound-free and free-free contributions to the LiHe red-wing emission, when taken to the semiclassical limit, has elucidated the approximations implicit in the quasistatic expressions. That work has indicated that the quasistatic model should be reliable for the lighter alkali-rare-gas molecules such as NaNe and NaHe. Furthermore, we have determined, by using a technique identical to that described in this report, potential curves for the $X^2\Sigma^+$ and $A^2\Pi$ states of NaHe. Our results of $D_e = 160(20) \text{ cm}^{-1}$ at $R_e = 5.1(1)a_0$ are in excellent agreement with the values of D_e (145 cm^{-1}) and

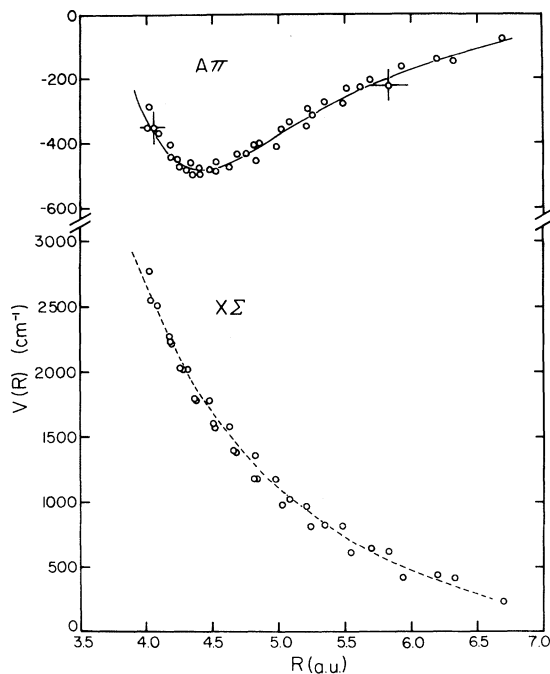


FIG. 2. Potential curves for the $X^2\Sigma$ and $A^2\Pi$ states of the NaHe molecule. Data points, this work, Solid line, Morse potential fit to the $A^2\Pi$ state. Dashed line, model potential result of Hanssen, Ref. 9. The radial scale is fixed at $R(\lambda = 7000 \text{ \AA}) = 4.18a_0$.

R_e ($5.1a_0$) determined by Lapatovich and co-workers^{5,10} from the rotationally resolved NaNe X-A absorption spectrum. This agreement, obtained between results determined from dramatically different analyses of NaNe data, establishes that classical approaches to the deconvolution of far-wing spectral line-shape data can in fact yield reliable potential curves for the lighter alkali-rare-gas pairs.

Our results for the NaHe $X^2\Sigma^+$ and $A^2\Pi$ state potential curves are presented in Fig. 2. The error bars on the energy values reflect the uncertainty in the bulb temperature, while those on the radial scale are determined from the uncertainty in the infinite temperature spectrum $I_N(\nu, \infty)$. The $A^2\Pi$ state potential is well fitted by a Morse function and the $X^2\Sigma^+$ repulsive potential by the function $A \exp(-BR)$, with $A = 61\,049 \text{ cm}^{-1}$ and $B = 0.799a_0^{-1}$. Our results for the Morse potential fit are presented in Table I, along with several recent theoretical results for the $A^2\Pi$ well depth and equilibrium separation. Our results for D_e and R_e are seen to be in reasonable accord with the Hartree-Fock calculations of Krauss¹³ and with the model potential calculations of Hanssen,⁹ but to differ dramatically from the pseudopotential results of Pascale and Vandepanque,¹¹ and from the model potential determination of Bottcher.¹²

Our result for D_e is more than twenty times the bound obtained by York, Scheps, and Gallagher,¹ who studied the pressure dependence of the NaHe red wing. From the absence of a pressure dependence in the 40–1000 Torr range these workers concluded that the NaHe A-state well was at most very weakly bound. It has been suggested⁵ that the lowest pressures in similar experiments on NaNe were not low enough to avoid a significant fraction of bound (NaNe)*. Our observation of a strong pressure dependence at lower temperatures and our determination of a rather deep well for NaHe argue that the same must have been true in the experiments on this molecule.

TABLE I. Depth and location of well minima for the NaHe $A^2\Pi$ state.

	D_e (cm^{-1})	R_e (a_0)	β (a_0^{-1})
This work	480(50)	4.4(2)	1.04(4)
Hanssen (Ref. 9)	299	4.58	...
Pascale (Ref. 11)	32	6.2	...
Bottcher (Ref. 12)	970	3.0	...
Krauss (Ref. 13)	210	4.53	...

The NaHe A -state well must be largely thermalized at 403 °K for as low a pressure as 40 Torr.

Our result is a reversal of the well-established trend of decreasing $A^2\Pi$ state well depth as one goes from NaXe to NaNe (decreasing rare-gas polarizability). The agreement between our results and those of Krauss¹³ indicates that the physical picture suggested by their calculations is correct: The attractive nature of the $A^2\Pi$ state is due to the deep penetration of the Na $3p$ orbital by the He atom. The penetration, which results in a Rydberg-like bond for the $A^2\Pi$ state, is due largely to the absence of a filled p shell in He. It would not be expected to occur for the heavier rare gases, which do have filled p shells. The strong decrease, in NaHe, of the repulsive part of the Na-rare-gas interaction is thus responsible for the reversal noted above. We expect that this effect, heretofore unestablished, will occur generally in the interaction of He with all the alkalis in their first p states.

In summary, our work on NaHe has determined a remarkably large well depth and range for the NaHe $A^2\Pi$ state potential and has established the Rydberg-like nature of the bond. This result has established the importance of the structure of the rare-gas atom in determining the repulsive part of the alkali-rare-gas interaction. It thus represents a significant advance in our understanding of the alkali-rare-gas diatomics. As a secondary result we have shown, through our results on NaNe, that the quasistatic theory is applicable to analyses of the spectra of the lighter

alkali-rare-gas pairs.

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