Perturbations in the $A^1\Sigma_u^+$ state of Na₂*

P. Kusch

The University of Texas at Dallas, P.O. Box 688, Richardson, Texas 75080

M. M. Hessel

National Bureau of Standards, Division 277.05, Boulder, Colorado 80302
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The observation of a magnetic rotation spectrum[1,2] for the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ spectrum of Na₂ and K₂ indicated that there were perturbations in the $A^1\Sigma_u^+$. Mulliken[3] postulated that an $a^3\Pi_u$ manifold lies near the $A^1\Sigma_u^+$ state and Carroll suggested[2] that the perturbing state is an $a^3\Pi_0$. No direct observations of optical transitions between the $^3\Pi$ and the ground state have been made since this is a "forbidden" singlet–triplet transition. Through absorption spectroscopy, we have directly observed the $A^1\Sigma_u^+$ to be perturbed. These observations indicate the perturbations are caused by the $a^3\Pi_0$, $a^3\Pi_1$, and $a^3\Pi_2$ states of Na₂.

The $A-X$ absorption spectrum of Na₂ has been photographed on the 9.3 m concave grating spectrometer of the Argonne National Laboratory. The constants that describe the X state are known with high precision through our analysis[4] of the $B-X$ band system. It was then possible to identify extended P and R branches in the $A-X$ system through $v' = 13$ and with J' up to 88 by use of the criterion that $R(J''-1) - P(J''+1)$ must agree with values found in the analysis of the $B-X$ system. An

TABLE I. Dunham coefficients of the $A^1\Sigma$ state of Na₂ (cm⁻¹).[a]

Y_{00}	1.4680541×10^4
Y_{10}	1.1731643×10^2
Y_{20}	$-3.5510555 \times 10^{-1}$
Y_{30}	$-1.7462516 \times 10^{-5}$
Y_{01}	1.1091903×10^{-1}
Y_{11}	$-5.8605589 \times 10^{-4}$
Y_{21}	2.1381859×10^{-6}
Y_{02}	$-3.7657992 \times 10^{-7}$
Y_{03}	$3.2246384 \times 10^{-13}$

[a]These coefficients were determined from a least squares fit of data covering the range $v' = 0$ to 20 and J' up to 88.
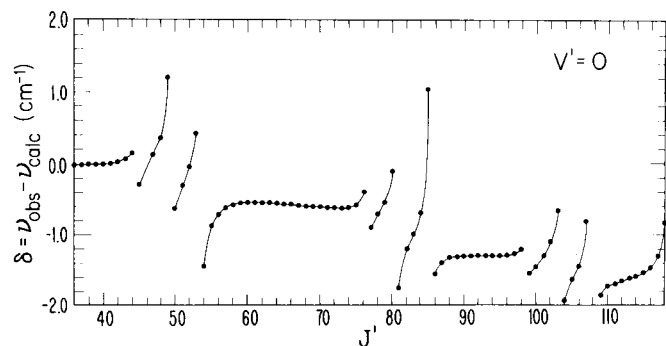
FIG. 1. Differences between observed and calculated line frequencies in the A state of Na_2 for $v' = 0$.

additional criterion for the choice of lines was that they should occur in a reasonably smooth series. The data thus found were subjected to a least squares analysis to determine the constants that describe the A state. It was at once evident that a fair number of R, P pairs could not be represented, within experimental uncertainty, by the conventional Dunham expression for the energy levels of the A state. These pairs were rejected, and a new representation of the energies of unperturbed or only slightly perturbed levels of the A state was found. The preliminary molecular constants for the A state are given in Table I. The detail with which the constants are given carries no implication of the uncertainty of the constants. More detailed analysis will almost certainly modify the present molecular constants. However, the frequencies predicted by use of these constants and the precisely known constants of the X state serve as a useful base from which to work.

R and P transitions to a *particular* v' and J' in A may occur with significant intensity from a considerable number of ground vibrational states, v'', and rotational states, J''. In searching for lines whose frequencies do not fall within the values calculated from the A and X state molecular constants, we require that all lines with the same v' and J' deviate equally, within experiment accuracy, from the calculated frequencies. The constancy of the deviation is independent of uncertainties in the predicted frequency of the levels in A.

In Fig. 1 are shown the results of our analysis for v' $=0$ and $36 \leq J' \leq 118$. The crucial quantity is $\delta = \nu_{obs}$ $- \nu_{calc}$. Each point in the figure describes the mean value of that quantity as observed for an average of 10
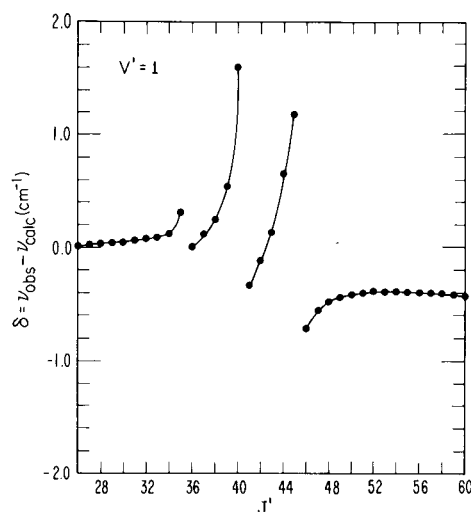

FIG. 2. Differences between observed and calculated line frequencies in the A state of Na_2 for $v' = 1$.

lines. The uncertainty in each δ is less than 0.010 cm^{-1}. The data extend down to $J' = 10$ but are not displayed below $J' = 36$ since the δ in the region below $J' = 36$ are all very nearly equal to zero.

A portion of a similar curve for $v' = 1$ and $26 < J' < 60$ is shown in Fig. 2.

In each of the three major perturbations for $v' = 0$ and for the perturbation in $v' = 1$, there are three discontinuities in δ. Kovacs and Lagerqvist[5] discuss the perturbation of $a^1\Sigma$ by $a^3\Pi$. They show that for Hunds case b the $^3\Pi_0$, $^3\Pi_1$, and $^3\Pi_2$ components can mix with the $^1\Sigma$ state and cause three discontinuities.

We tentatively assign the observed discontinuities to the three components of the $^3\Pi$ state. Further analysis is required to test this hypothesis and to determine the properties of the $^3\Pi$ state.

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