Identification of Rydberg States in Na$_2$ by Two-Step Polarization Labeling

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Ten new excited $^1\Delta_g$ states and five new excited $^1\Pi_g$ states of Na$_2$ have been identified with the use of the two-step polarization labeling technique. The electronic energies of these states form a molecular Rydberg series. By extrapolating the dissociation energies, vibrational constants, and rotational constants of these Rydberg states it is possible to obtain good estimates of the same quantities for the $X^2\Sigma_g$ ground state of Na$_2{}^+$.

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In recent years, the Rydberg states of the atoms have been the subject of many experiments. However, over the last fifty years the Rydberg states of only a few diatomic molecules have been studied.[1] The vibrational-rotational structure of molecules complicates the electronic absorption spectra considerably. However, the absorption spectrum of a molecule can be greatly simplified by use of polarization labeling because transitions from only one selected vibrational-rotational level are observed.

The technique of two-step polarization labeling[2] has been demonstrated to be an extremely effective tool for the study of excited states in diatomic molecules. As in polarization spectroscopy,[3] a resonant polarized pulsed pump laser induces an optical anisotropy in the levels of a single vibrational-rotational transition. A broadband linearly polarized pulsed probe laser will experience a change in polarization for frequencies resonant with transitions which have a common level with the pump-laser transition. If the probe is passed through a crossed polarizer, only those frequencies which interacted with a level of the pumped transition will be transmitted. A spectrograph can then be used to record the probe spectrum photographically. The absorption spectrum is greatly simplified because probe signals can

only occur from the two levels of the pump transition. Therefore, P-, Q-, and R-branch transitions can be readily identified.

Probe signals corresponding to transitions from the upper level of the pump transition to higher excited states can be distinguished from absorption of oriented ground-state molecules by the absence of two-step signals on a delayed probe spectrum.[2] Alternatively, dipole selection rules for the oriented molecules, and the different vibrational-rotational constants, provide ways to recognize new states.[4] The use of a broadband probe makes it possible to cover large regions of the optical part of the spectrum on a single photographic plate. This is very useful when searching for new excited states, since several different vibrational bands of an excited state will appear on a single plate. Such vibrational sequences yield immediate information about the vibrational-rotational structure of the excited state.

In this experiment, single vibrational-rotational transitions in the X-B band of Na$_2$ (Ref. 5) were labeled by the pulsed pump laser. A series of broadband probes which covered the region from 7000 to 5500 Å were used to probe transitions to higher excited states. In Fig. 1, a typical probe spectrum is shown. The long bright lines
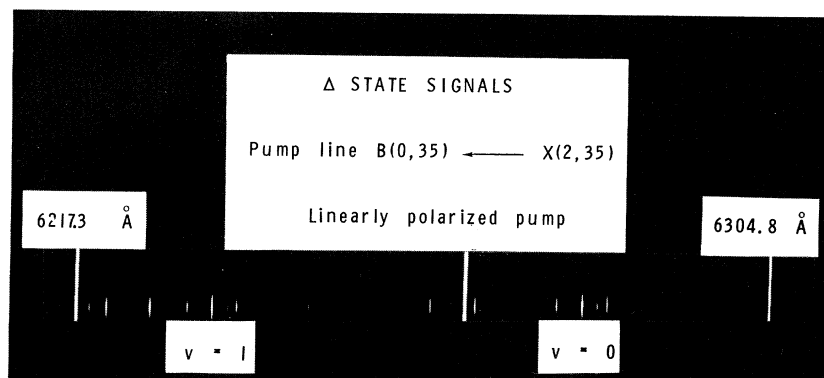

FIG. 1. Probe spectrum showing transitions to a $^1\Delta_g$ state.

are neon reference lines, used to measure the probe signals with an accuracy of 0.2 cm^{-1}. This spectrum shows two distinct vibrational sequences. One of these sequences shows P-, Q-, and R-branch transitions from the upper level of the pump transition to the two lowest vibrational bands of a $^1\Delta_g$ state. The $^1\Delta_g$ state was identified as such by the intense Q-branch signals observed in the probe spectrum. For the pump and probe wavelengths used in this spectrum, Q-branch signals could only occur for a Π-Δ transition.[4] The other sequence shows P- and R-branch transitions from the lower level of the pump transition to two vibrational bands of the $A^1\Sigma_g{}^+$ state. From this spectrum and others like it, it was possible to identify ten new $^1\Delta_g$ states and five new $^1\Pi_g$ states.

With use of the separated-atom approach,[6] molecular Rydberg states of Na_2 can be thought of as being created by bringing together a ground-state sodium atom and a sodium atom in an excited state. Such a state of the Na_2 molecule will consist of a single electron orbiting a molecular core in the ground state of $Na_2{}^+$. Because of the axially symmetric field of the core, the orbital angular momentum of the outermost electron will precess about the internuclear axis and its projection along the internuclear axis will be a constant of the motion. The projection of the electronic angular momentum is designated by the quantum number λ. Therefore, a molecule in such an excited state can be characterized by the quantum numbers n, l, and λ. In this model, λ is an exact quantum number. However, because of the axially symmetric field n and l are approximately good quantum numbers. If the outer electron does not penetrate the core, then to first order the electronic energy of the system is due to the interaction of the outer electron with the monopole and quadrupole fields of the core and the polarization of the core by the outer electron. By use of hydrogenic wave functions, the energy levels of such a system are given by[7]

$$T_0(n) = T_\infty - R/n^2 - RC_{l\lambda}/n^3 - RD_{l\lambda}/n^5.$$

In this relation R is the Rydberg constant, T_∞ is the ionization limit, and the coefficients $C_{l\lambda}$ and $D_{l\lambda}$ depend on l and λ and are directly related to the quadrupole moment and polarizabilities of the core. The above model must be regarded as a rough approximation, since it does not account for penetration of the core and is only a first-order expression.
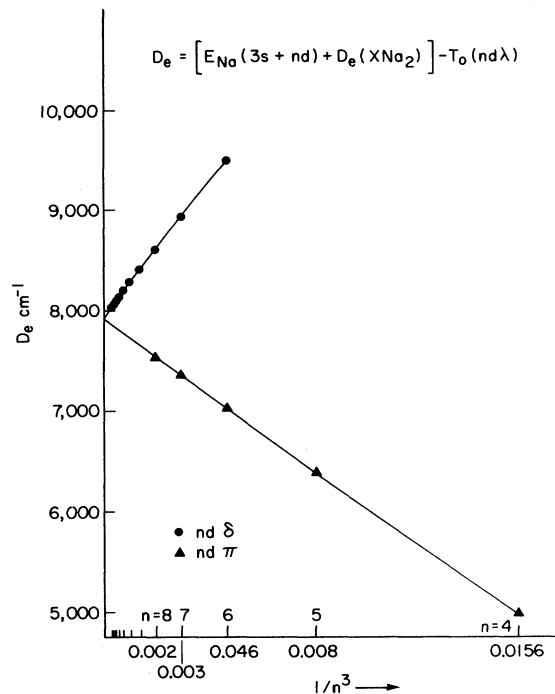
By fitting the term values of the vibrational-

FIG. 2. Extrapolation of the dissociation energies of the Rydberg states.

rotational levels of the excited states with the Dunham expansion, it was possible to determine the electronic energy and the vibrational and rotational constants of the observed excited states. In the molecular-orbital approach, the observed $^1\Delta_g$ and $^1\Pi_g$ states correspond to $KKLL$-$(3s\sigma)(nd\delta)$ and $KKLL(3s\sigma)(nd\pi)$, respectively. The assignment of the principal quantum numbers was determined by the best fit of the electronic energies to relation (1). With the assignment of $n = 6$–15 for the $nd\delta$ series and $n = 4$–8 for the $nd\pi$ series, the electronic energies calculated from the fit of relation (1) agree with the experimental values of the electronic energies to within 3 parts in 10^5. In Fig. 2, the dissociation energies of the $nd\delta$ and $nd\pi$ states are plotted as a function of $1/n^3$. The points represent the experimental values and the curves represent the result of the fit of relation (1). Both curves extrapolate to the y axis and give values of the dissociation energy of the ground state of $Na_2{}^+$ which differ by only about 4 cm^{-1}. In Table I, the average of these values is compared with other values for the dissociation energy from extrapolation of the electronic energies of the B, C, and D states,[8] and photoionization from the

TABLE I. Comparison of values for the dissociation energy, D_e, of the ground state of Na_2^+.

	D_e (cm^{-1})
This work	7935 ± 5
Hudson (Ref. 9)	7824 ± 80
Barrow et al. (Ref. 8)	8138 ± 323

ground state of Na_2.[9]

The bonding effects of the outer electron are illustrated nicely in Fig. 2. From molecular-orbital theory, a δ_g orbital is a bonding orbital and a π_g orbital is an antibonding orbital. The dissociation energy of the $nd\delta$ states decreases as n increases, indicating that the bonding effect of the outer δ_g electron decreases as it interacts less with the core. Conversely, the dissociation energy of the $nd\pi$ states increases as n increases, indicating that the effect of the antibonding π_g electron decreases as it interacts less with the core.

It is also possible to obtain estimates of the vibrational and rotational constants of the ground state of Na_2^+ by extrapolation of the constants of the Rydberg states. As the principal quantum number increases, the outer electron interacts less with the core and so the vibrational-rota-
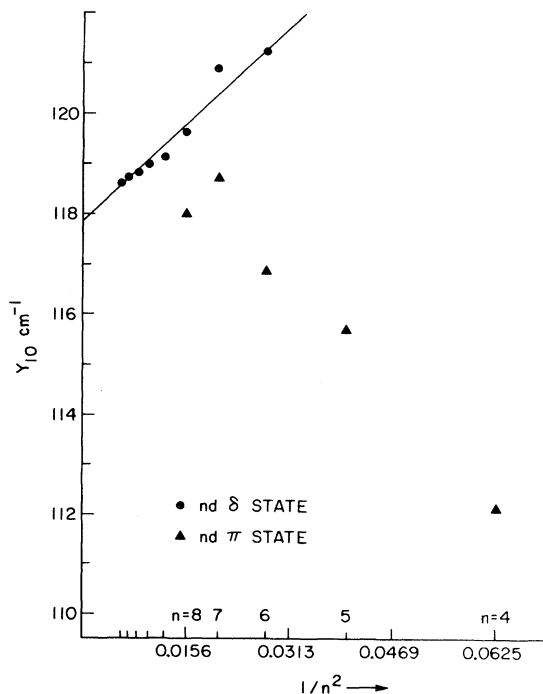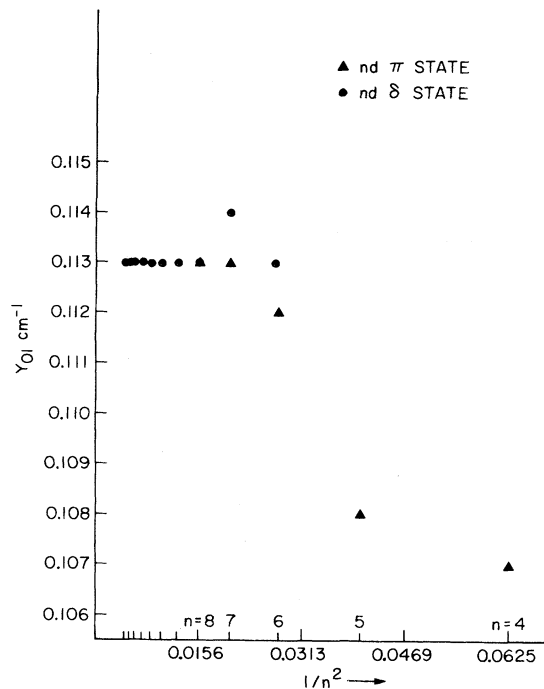

FIG. 4. Extrapolation of the rotational constants of the Rydberg states.

tional structure of the Rydberg states should approach that of the ground state of Na_2^+. In Figs. 3 and 4, the vibrational (Y_{10}) and rotational (Y_{01}) constants of the $nd\delta$ and $nd\pi$ states are plotted versus $1/n^2$. It can be seen that as n increases both the $nd\delta$ and $nd\pi$ states converge to roughly the same values. In Table II, the extrapolated constants of the ground state of Na_2^+ are compared to theoretical constants.[10,11]

Future studies of molecular Rydberg states with use of two-step polarization labeling look very promising. The work on Na_2 is still continuing in an effort to identify $ns\sigma$ and $nd\sigma$ states. Now that molecular Rydberg states have been identified, it would be interesting to study some of their properties in more detail. With use of an Na_2 beam and two tunable dye lasers, it should

FIG. 3. Extrapolation of the vibrational constants of the Rydberg states.

TABLE II. Comparison of extrapolated and theoretical vibration constant, Y_{10}, and rotational constant, Y_{01}, of Na_2^+.

	Y_{10} (cm^{-1})	Y_{01} (cm^{-1})
Extrapolation	118	0.113
Bardsley et al. (Ref. 10)	126	0.117
Bertoncini et al. (Ref. 11)	116	0.106

be possible to produce a substantial population
in a single vibrational-rotational level of a Ryd-
berg state. Phenomena such as superradiant or
microwave transitions, autoionization, and field
ionization could then be studied.

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Linear Electro-Optic Effect in Gases

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The *linear* effect of an electrostatic field on the intensity of scattering of light by gas is
reported. The change in the depolarized intensity scattered by gaseous methyl chloride in
the y direction from a beam of right circularly polarized light propagating in the z direc-
tion due to an electrostatic field $F_x = 7 \times 10^6$ V m^{-1} is -7 ± 1 ppm. It changes sign on re-
versing F_x, the direction of scattering, and the circularity of the light. The effect should
be exhibited by all materials.

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Crystals may exhibit linear electro-optical
properties, but gases and liquids are expected
to show quadratic effects of an electric field on
their optical properties. However, we report a
linear effect of an electric field on the intensity
of light scattered from a circularly polarized
beam by gaseous methyl chloride; the differential
scattering is of opposite sign in right- and left-
circular polarization (Fig. 1).

In 1846 Faraday observed a linear effect of a
magnetic field on optical rotation.[1] Magneto-
optical rotation was later shown to be a property
possessed by all materials. We believe that all
substances also have a linear electro-optical
scattering power.[2]

Figure 2 shows the apparatus. Argon-laser
radiation at 488 nm was circularly polarized by
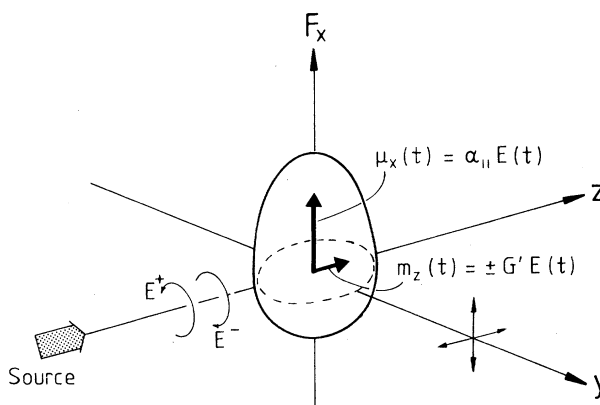a Pockels cell and focused into the cell. An elec-

FIG. 1. A polar molecule such as CH$_3$Cl oriented by
the electric field F_x. The scattering from right (E^+)
and left (E^-) circularly polarized light with x or z
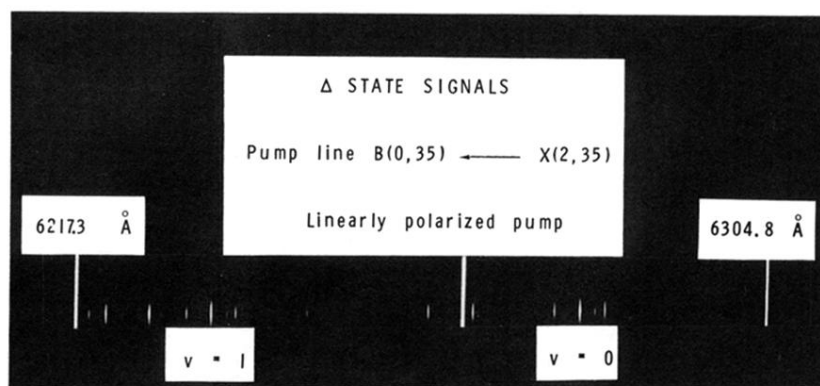polarization is observed on the y axis.

FIG. 1. Probe spectrum showing transitions to a $^1\Delta_g$ state.