Ionization and Energy Pooling in Laser-Excited Na Vapor

G. H. Bearman and J. J. Leventhal
Department of Physics, University of Missouri at St. Louis, St. Louis, Missouri 63121
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We have observed ion formation (both Na^+ and Na_2^+) and radiation from high-lying Na states when low-density vapor ($\sim 10^{13}$ cm^{-3}) is irradiated with a cw dye laser tuned to one of the D lines. The Na^+ ions probably result from photodissociation of Na_2^+ formed by Na($3p$)-Na($3p$) associative ionization, while the high-lying radiating states are formed in energy-pooling reactions.

Within the last few years tunable dye lasers have been extensively used to investigate a variety of atomic and molecular processes.[1-3] The alkali metals are often studied because of their strong resonance absorption and the accessibility of their resonance lines to contemporary dye lasers. Recently several anomalous effects have been observed in studies involving photoexcited alkali-metal vapors. In separate experiments, McIlrath and Lucatorto[4,5] observed nearly complete ionization of Na and Li vapors (yielding atomic ions) using a 1-MW pulsed laser. Using a cw dye laser Allegrini *et al.*[6] observed radiation from states lying higher than the photoexcited $3p$ level. Of particular interest is their observation of radiation from states lying higher than twice the $3s$-$3p$ energy. It has been suggested that the ionization results from electron impact on Na($3p$) where the necessary electronic kinetic energy is supplied by e-Na($3p$) superelastic collisions.[5,7,8] The initial seed electrons are presumed to be provided by either two-photon ionization

$$\mathrm{Na}(3p) + 2\hbar\omega \rightarrow \mathrm{Na}^+ + e\,, \tag{1}$$

or laser-induced ionization

$$\mathrm{Na}(3p) + \mathrm{Na}(3p) + \hbar\omega \rightarrow \mathrm{Na}^+ + \mathrm{Na} + e. \tag{2}$$

This latter process was treated theoretically by Geltman[7] who suggested that the radiation observed by Allegrini *et al.*[6] was from electron-impact excitation, again from superelastically heated electrons.

We have observed similar anomalous effects under different experimental conditions. Since these effects can complicate experiments involving optically pumped Na, it is important to understand the production mechanisms. In this Letter we report simultaneous observation of both ionization and radiation produced by a cw dye laser. Our Na-atom density is much lower than that of McIlrath and Lucatorto (10^{13} cm^{-3} vs 10^{16} cm^{-3}) as is our laser power density. Atom densities comparable to ours were present in the experiments of Allegrini *et al.*; however, ion formation could not be observed with their apparatus. Mass analysis shows that under our experimental conditions both Na_2^+ and Na^+ are formed, in the ratio of ~ 10:1. The Na_2^+ ions are formed by collision processes in the vapor cell and do not result from ionization of the Na_2 dimer. We believe that our new data contribute to further clarification of the mechanisms leading to the apparently anomalous effects.

The experiments are performed by irradiating sodium vapor in an open-ended stainless-steel cell with a jet-stream dye laser. The cell was a 2.5-cm-long, 6-mm-diam cylinder with 3-mm-diam holes in each end; the laser beam was coaxial with the cell. Sodium vapor was provided by an oven located below the vapor cell to minimize blackbody radiation. The dye laser power was ~ 1 W, the linewidth ~ 40 GHz, and the power density ~ 10^2 W/cm^2. Photons exit the vapor cell through a slot parallel to the laser beam and enter a 0.25-m scanning monochromator. Optical spectra were obtained by counting pulses from a cooled photomultiplier tube; a notch filter reduced the detected resonance fluorescence by ~ 10^7. Opposite the photon exit slot is a 3-mm-diam hole for sampling ions with a quadrupole mass filter; an ion-focusing lens was interposed between the cell and the mass filter. A particle multiplier operating in the counting mode was the ion detector; mass spectra were obtained by scanning electronically and storing the signal in a multichannel scalar.

The atom density in the cell was determined by electron impact, instead of vapor pressure versus temperature curves. This was felt necessary because of nonequilibrium conditions in the cell. Comparison of Na^+ and Ne^+ ion signals using a known Ne pressure (Ne was used to minimize mass-discrimination effects), together with known electron-impact ionization cross sections,[9,10] yielded a Na-atom density of ~ 10^{13} cm^{-3}. For

the dimensions of the cell and this Na density only single Na-Na collisions should be important unless some process has an extraordinarily high cross section. At these sodium densities the dimer density is calculated to be $\lesssim 1\%$ that of the Na atoms.[11]

Figure 1 shows an optical spectrum obtained with the laser tuned to the Na D_1 line (5889.95 Å). In addition to the resonance fluorescence, radiation from the $4p$, $5p$, $5s$, and $4d$ states, was observed. As shown in the Grotrian diagram of Fig. 1, two of these states have energies above $2\hbar\omega$ ($\hbar\omega$ = energy of a 589-nm photon). All spectral features disappear when the laser is tuned off resonance. No radiation from Na_2 was observed, although there are several band systems in the optical region. We did not observe radiation from the two highest states reported by Allegrini *et al.* ($6s$ and $5d$), but we did observe radiation from Na($5p$) which was not reported in Ref. 6.

In order to ensure that ions are not produced by electron impact in the mass filter, the cell was grounded and the ion lens kept at $V_Q \sim -2$ V. When mass spectra were taken with V_Q positive no ions were observed, indicating that the ions were formed in the cell. To estimate the ion-collection efficiency we used the known e-Ne ionization cross section[9] together with the electron current, Ne^+ current, and Ne gas pressure. From the mass filter efficiency the fractional ionization is estimated to be $\sim 10^{-5}$ for Na^+. Thus, the degree of ionization observed here is considerably lower than in the experiments of McIlrath and Lucatorto. Furthermore, they detected only atomic ions while Na_2^+ is the dominant ion produced in our experiment. These Na_2^+ ions are probably formed by Na($3p$)-Na($3p$) associative ionization as observed by von Hellfield, Caddick, and Weiner,[12] rather than photoionization of Na_2.

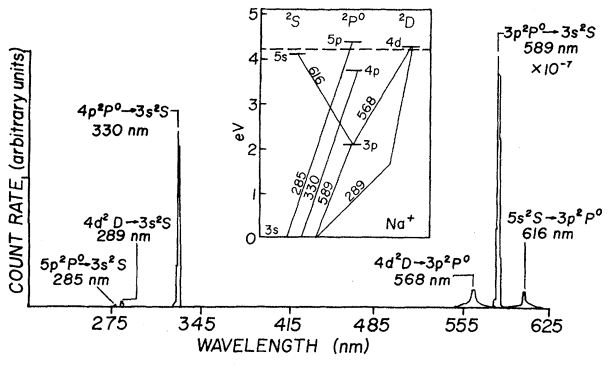

FIG. 1. Optical spectrum (uncorrected) obtained with the laser tuned to Na $D1$. Na I states observed in emission are indicated in the Grotrian diagram. The dashed line indicates twice the Na($3p$) energy.

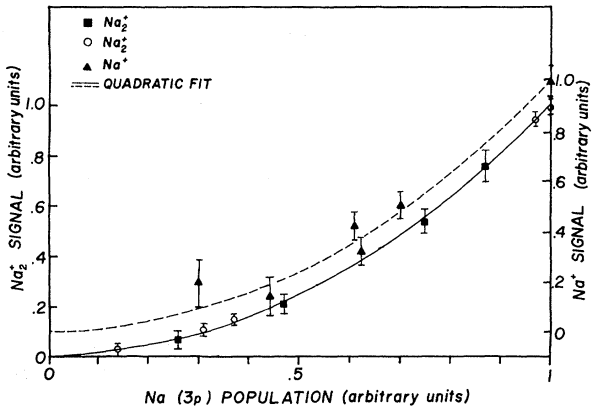

FIG. 2. Na^+ and Na_2^+ ion signals as functions of Na($3p$) population. Data were taken for Na_2^+ at two different Na atom densities: squares, 5×10^{13} cm^{-3}; circles, 3×10^{13} cm^{-3}. Note that the zeros on the ordinates are shifted.

Figure 2 shows the Na^+ and Na_2^+ ion signals as functions of Na($3p$) population; the Na($3p$) population was changed by slightly detuning the laser. For both ions the dependence is approximately quadratic indicating that Na($3p$)-Na($3p$) processes are important. Figure 3 illustrates the behavior of the ion signals when various gases were added to the cell. The behavior of each ion as a function of pressure was independent of gas for the

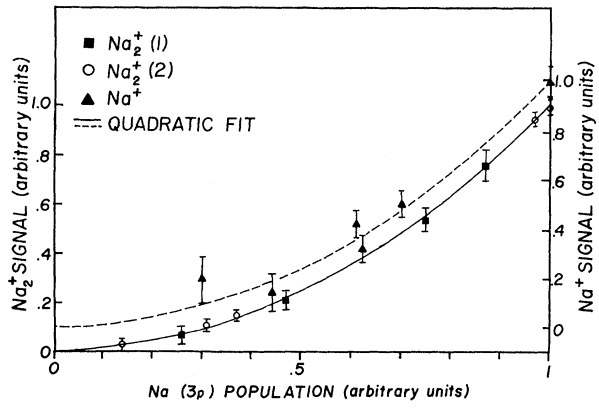

FIG. 3. Na^+ and Na_2^+ ion signals as functions of pressure of various additive gases. Data are normalized to constant Na($3p$) population. The Na^+ data were taken only with N_2. The arbitrary ordinates for Na_2^+ and Na^+ are unrelated.

five gases added, suggesting that the enhancement of Na^+ and the decrease of Na_2^+ depend on the presence of a third body rather than the nature of the gas.

If superelastically heated electrons are present in the cell then the radiation and the Na^+ ions could both result from electron-impact processes. However, at the atom densities of our experiments the electron mean free path through Na($3p$) is about 25 cm, roughly 40 times the cell diameter, so it seems unlikely that any appreciable heating by multicollisional processes could occur. This mean free path was estimated from the Na atom density and the $e + \mathrm{Na}(3p) \rightarrow \mathrm{Na}(3s)$ cross section (~ 80 Å^2).[5,13] To check for the presence of hot electrons, potassium was added to the oven. Both K^+ and NaK^+ were observed, but no K I radiation was detected. The K^+ ions are probably the result of exothermic Na^+-K charge transfer while the NaK^+ is probably formed in a laser-induced Na($3p$)-K($4s$) process.[12] From the $4s \rightarrow np$ electron-impact cross sections,[14] the K-atom density, and the known efficiency of the optical system it is calculated that if 3–5 eV electrons are present the $4p \rightarrow 4s$ K I resonance line (770 nm) count rate should be about 10^3 times the background; the $5p \rightarrow 4s$ (405 nm) count rate should be about 5×10^3 times the background. The absence of these lines eliminates the possibility that hot electrons play an important role in our experiments. Since the atom densities and laser power densities of the experiments of Allegrini *et al.*[6] were similar to ours, it may be inferred that hot electrons did not contribute to their observations. However, our results do not rule out hot electrons in the experiments of McIlrath and Lucatorto, since they observed almost total ionization with considerably higher atom and laser power densities.

Using the information in Ref. 7 it is possible to estimate the fractional ionization expected from processes (1) and (2) for our experimental conditions. For two-photon ionization the ratio of Na^+ to neutral-atom densities would be about 10^{-14}, while laser-induced ionization should yield about 10^{-12}; these ratios are orders of magnitude lower than the estimated fractional ionization (10^{-5}) in the experiment. An additional source of Na^+ is photodissociation of the Na_2^+ that are formed by associative ionization. An estimate of the Na^+/Na_2^+ ratio based on a calculated cross section[15] and the assumptions that Na^+ are formed only by photodissociation and lost only by drift out of the "laser cylinder" yields a value of 0.003; the observed ratio is 0.1. If it is assumed that Na_2^+ ions are formed only by associative ionization and lost by both drift and photodissociation, the Na_2^+ ion concentration is $\sim 10^{24}\sigma$ cm^{-3}, where σ is the associative ionization cross section in square centimeters. For $\sigma = 10^{-15}$ cm^2 the fractional Na_2^+ ionization is close to the experimental value, and the Na^+ fractional ionization a factor of ~ 30 lower than the experimental value. However, since this is much closer to the observed value than estimates based on either processes (1) or (2) it is considered likely that photodissociation is the major source of atomic ions. Experimental uncertainties that could contribute to the difference include ion-collection efficiency and determination of the atom density, spot size, and power density.

Production of high-lying Na(nl) can result from energy-pooling Na($3p$)-Na($3p$) collisions, where formation of states higher than $2\hbar\omega$ requires conversion of kinetic energy. If so, the lines originating in these states ($4d$ and $5p$ in our work) should be relatively weak. As shown in Fig. 1, this is indeed the case. The maximum energy defect (above $2\hbar\omega$) observed in our experiments is 0.14 eV which is about three times thermal at 500°K. At this temperature, about 10% of the atoms have kinetic energies in excess of 0.14 eV so that conversion of kinetic to internal energy seems possible. On the other hand, Allegrini *et al.* observed excited states lying as high as 0.4 eV above $2\hbar\omega$; less than 0.1% of the atoms have enough kinetic energy to make up this deficit. In further contrast to the results of Allegrini *et al.*, we observed no enhancement of the Na I line signals when Ne gas was added. In fact, we observed no change in the Na I radiation when unreactive gases (Ne, Ar, or N_2) were added. This last suggests that third-body kinetic energy does not play a role in the production of Na(nl).

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Molecular-Photoelectron Angular Distributions as a Probe of Dynamic Symmetry Breaking

Dan Dill and Scott Wallace
Department of Chemistry, Boston University, Boston, Massachusetts 02215

and

Jon Siegel and J. L. Dehmer
Argonne National Laboratory, Argonne, Illinois 60439

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Molecular-photoelectron angular distributions are shown to depend qualitatively on symmetry-breaking hole localization during inner-shell photoionization. This is illustrated by comparing localized and delocalized calculations of the asymmetry parameter $\beta(\epsilon)$ for K-shell photoionization of N_2 in the vicinity of the f-type shape resonance at approximately 10 eV above threshold. Comparison with the isoelectronic CO shows that the K-shell $\beta(\epsilon)$ for N_2, in the localized treatment, resembles that for the K shell of oxygen rather than carbon in CO.

Ionization of molecular core states which are distributed on two or more equivalent atomic sites can lead to states of the residual ion in which the vacancy is effectively localized on a single equivalent site, prior to becoming filled by Auger or radiative decay. In this Letter we show that the lowering of molecular symmetry accompanying hole localization during the photoionization process (dynamic symmetry breaking) has a dramatic effect on the spectral variation of molecular-photoelectron angular distributions. This effect can be traced to additional couplings in the final state, induced by the lowered symmetry of the molecular core. Hence, photoelectron angular distributions probe the effects of hole localization on the ejected-electron wave function, and thus complement the evidence based on the total energy of the ionic hole state first described by Bagus and Schaefer.[1]

To illustrate the effects of dynamic symmetry breaking on inner-shell photoionization, we calculated the integrated cross section and photoelectron asymmetry parameter for K-shell photoionization of N_2 in the vicinity of the f-type ($l=3$) shape resonance at ~10 eV kinetic energy.[2-7] The calculations were performed using the continuum–multiple-scattering model,[8,9] and will be described fully elsewhere.[10] Briefly, the delocalized-case calculations were performed as before[4,5] with both the initial and final state calculated in the same self-consistent-field ground-state potential based on Slater exchange with $\alpha = 1$. This is known[4,5] to reproduce the position of the σ_u shape resonance rather well. The localized-case calculation employed the same initial state but a final state generated from a potential in which the energy-dependent Hara-exchange[11,12] approximation was used. This model permits one to explicitly specify the configuration of the residual ion, which in this case is N_2^+ with an electron removed from the $1s\sigma$ orbital of one atom. Thereby the spectators explicitly deter-

