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Effect of Resonant Laser Light Upon a Fast-Atom Charge-Exchange Source

E. W. Rothe and B. P. Mathur

Research Institute for Engineering Sciences and Department of Chemical Engineering,
Wayne State University, Detroit, MI 48202, USA

G. P. Reck

Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

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Abstract. The effect of resonant laser-light upon a charge-exchange source of eV-range sodium atoms is to decrease the Na kinetic energy by about 2 eV. The mechanism probably involves a reduction of the space charge in the low-energy ion precursors. The reduction is caused by electrons created in collisional ionization of laser-excited atoms. This is related to the well-known optogalvanic effect. A knowledge of the existence of this effect can be important for the design of experiments involving laser driven chemistry.

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Collision studies of laser-excited species often use particle beams which have been electrically accelerated to a kinetic energy (KE) in the eV range. Here we describe a change of ~2 eV in the KE of sodium atoms which occurs when resonant laser light is directed into a fast-atom source.

Experimental

This KE change was observed in measurements of KE thresholds for ionization reactions. Fast Na originates in a widely used charge-exchange source for alkali atoms [1]. The source consists of an electrically grounded metal cell containing a) Na vapor, b) a 1/4 mm diam rhenium surface-ionization filament, and c) a grounded plane-grid located ~1/4 mm from the filament and parallel to it. The resistance-heated filament is maintained at a positive voltage V with respect to ground.

A simplified description of the source operation follows. Thermal Na atoms strike the filament, are ionized there to Na^+, which are electrically accelerated through the grid. Some energetic ions exchange charge with the Na vapor. The ion path in the cell is ~15 mm. This resonant charge-transfer results in negligible momentum change. Ions which leave the source are removed with condenser plates, while the Na beam consists of effusive and fast atoms.

Several laboratories [2], including ours, have studied cross sections in the near-threshold KE region, for ionization processes such as

$$\mathrm{Na} + \mathrm{M} \rightarrow \mathrm{Na}^+ + \mathrm{M}^-, \tag{1}$$

$$\mathrm{Na}^*(3p) + \mathrm{M} \rightarrow \mathrm{Na}^+ + \mathrm{M}^-, \tag{1a}$$

or

$$\mathrm{Na} + \mathrm{M} \rightarrow \mathrm{Na}^+ + \mathrm{A} + \mathrm{B}^-, \tag{2}$$

where M is a molecule, and A and B are fragments. For most M these reactions are endoergic and do not proceed at thermal energies. However, they are often efficient with fast sodium atoms.

We distinguish between the true cross section $\sigma_{\mathrm{cm}}(E)$, where E is the c.m. kinetic energy, and the effective (measured) cross section $\sigma(\mathrm{KE})$, which results when σ_{cm} is averaged over energy distributions in Na and M, and KE is the nominal Na kinetic energy in the laboratory system. If $\sigma_{\mathrm{cm}}(E)$ has a straight line section, and if the experimental energy spreads within that section are nearly Gaussian, and are less than the energy range of a

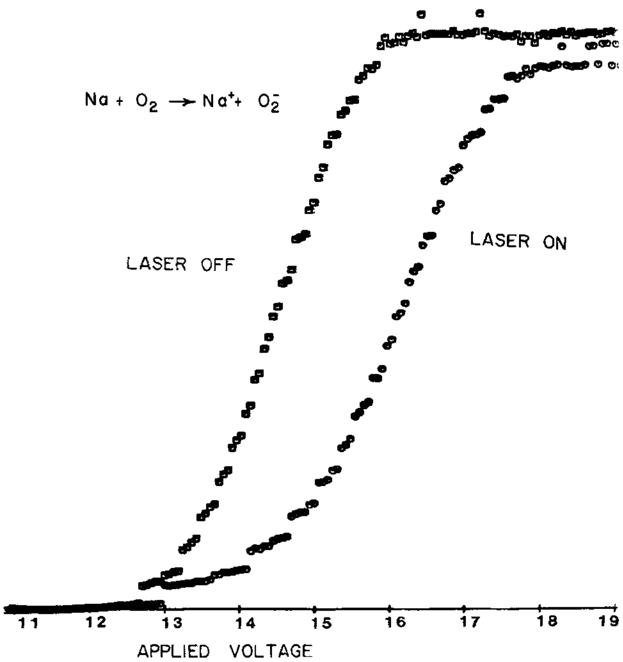

Fig. 1. Na$^+$ yields, obtained from $Na + O_2 \rightarrow Na^+ + O_2^-$, as a function of the Na kinetic energy. Results are with, and without, resonant laser light which is antiparallel to the Na beam. The abscissa is not calibrated (see text), and is ~5V greater than the KE. Voltage *differences* are accurate, and are equal to Na kinetic energy differences in eV

straight-line section of $\sigma_{cm}(E)$ (these conditions are often well approximated), then energy averaging of $\sigma(E)$ will yield equal positive and negative contributions and σ(KE) will also be nearly straight. Figure 1 displays a typical σ(KE).

Reaction (1a) can be studied with the use of laser excitation. Use of the D lines yields Na* (either $3^2P_{3/2}$ or $3^2P_{1/2}$). We had originally intended to compare reactions (1) and (1a), and that experiment led to the observations reported here, as well as to the primary result [that reaction (1a) has a lower threshold than reaction (1)] which was previously published [3].

The Na* is formed by the use of light from a cw, multimode dye laser (Model 490, Coherent). We use either the D1 (589.6 nm) or the D2 (589 nm) resonance line, with ~1/2 *w* laser power. The light has about a 30 GHz frequency spread (~0.035 nm).

Except for the laser, the apparatus has been previously described [4]. In brief, a 2 mm diam Na beam intersects a low-density vapor of M. Either product cations or anions can be accelerated into a high transmission mass filter which is coaxial with the Na beam. The ions are mass analyzed and counted. Scans of the KE of the Na beam could be made with the laser on or off. (Results with no laser light and with off-resonant laser light, e.g., at 589.3 nm, were always equivalent.)

The laser beam is coaxial with, and antiparallel to, the Na beam. The 30 GHz spread means that neither hyperfine spread (~2 GHz) nor Doppler shift (~15.5 GHz at 10 eV) cause problems in excitation, although it does result in a small population fraction of Na*/Na.

We expected [3] that the threshold KE for reaction (1a) would be smaller than that for reaction (1) because Na* has 2.1 eV more internal energy. At the resonant wavelengths, which were easily identified via bright fluorescence from the beam, some of the expected Na$^+$ were observed below the threshold for reaction (1).

The KE was then raised 1–2 eV above the ground-state threshold, so that Na$^+$ were observed without laser light. Under these conditions the *addition of resonant laser light decreased the ion yield* by as much as an order of magnitude. The size of the reductions depended upon the identity of M, and the KE.

Similarly, ratios of intensities of M^-/B^-, obtained when both reactions (1 and 2) operate, change with the addition of resonant laser light.

We then did measurements of σ(KE) with and without resonant light. A typical result is shown in Fig. 1 for Na + O$_2$. The abscissa is a voltage which is applied to one lead of the dc-heated filament. This is ~5V larger than the absolute KE (in eV) because it has not been corrected for contact or plasma potentials, or for the ir drop along the filament and leads [1]. However, the difference in KE between the two curves is correct, and it is this quantity which is of interest here.

The basic experimental observation from these KE scans is that the *resonant laser light reduces the average* KE *of the beam atoms by about* 2 eV. A glance at Fig. 1 reveals the basis of the reduction of ion signal with resonant light that was described above. The M dependence of the reduction is primarily caused by different slopes of σ(KE). Similarly the M^-/B^- ratio change is caused by dissimilar σ(KE) for reactions (1 and 2).

The straight-line portions of the σ(KE) curves are used as monitors of KE-shifts primarily because that apparatus was already in place. In the next two paragraphs we compare some of the relevant aspects of this approach with those of more conventional methods.

We have previously used a mechanical velocity selector [1] and TOF [5] to energy analyze beams from this source. These two methods have also been used by others [6]. They yield absolute values of the KE: however, only changes in KE are required here. They also work in a large range of KE, while the present method is confined to a region within a few eV of the threshold for any particular M. This can be alleviated by using different M. TOF might yield more knowledge of the shape of the KE distribution. However, electrical source pulsing [5] may distort that distribution.

Another method is to measure the Doppler shift in absorption of a single-mode laser line [7]. In this case resolution in KE is degraded because of angular spreads in the Na beam. For example, for a nominal 45° intersection of laser and Na beams, a Na beam divergence of 50 mrad ($\sim 3°$), results in a spread of frequencies that corresponds to a velocity spread [7] $\Delta v/v$ of 0.05, and therefore $\Delta\text{KE}/\text{KE} \cong 0.1$. Accordingly, at a nominal KE of 10 ev, the resolution is ~ 1 eV, while a typical KE spread in the Na beam is 1/4 eV [1]. In contrast, the uncertainty in measuring KE shifts in the straight line portions of curves such as those in Fig. 1 is < 0.1 eV [1]. There is some additional KE spread introduced via the thermal energies of the target molecules [8]. However, as previously discussed, there is very little effect upon the straight line portion of $\sigma(\text{KE})$ (although it is very important in a threshold measurement [8]). Therefore, the experimental shift shown in data such as those in Fig. 1 is, to a very good degree of approximation, equal to the reduction in the beam KE. Appropriate deconvolution procedures would improve the precision of all these methods. Nevertheless, within the narrow range of energies available with any single M, the method used here has some advantages for the measurement of the average value of KE shifts. If a very well collimated beam were studied, the laser method would yield additional information about the form of the energy distribution.

The KE shift was reproducible and similar results were obtained with $\text{M} = \text{O}_2$, Cl_2, Br_2, NO_2, HF, HCl, SO_2, and SnCl_4. The range of KE for these M was from ~ 3–15 eV.

(Although Fig. 1 shows that the two curves are similar except for the shift of KE, closer examination shows that the laser-on curve has a less sharp threshold: i.e., additional ions are there. These come from reaction 1a via the small fraction of Na* in the beam, whose KE is also reduced by ~ 2 eV. If the laser-on curve were translated to higher energies, so as to compensate for the drop in KE, we would obtain data similar to that in [3]: i.e., a lower threshold for Na* reactions. Because the signals in the very near-threshold region are much smaller, greater care must be taken there, which was done in [3] and the data reported there are more precise in that region.)

The shift of KE was initially puzzling. We looked for explanations such as a) deceleration of Na in the beam region via multiple photon absorption, or b) closing of the reactive channel with Na*. The first of these was impossible because of known Na* lifetimes and beam velocities, and the second because only a small fraction of the Na atoms were excited. We then investigated the fast-atom source, where the laser beam terminated. In order to verify that a resonant interaction in the source was responsible, we measured the KE dependence of reactions analogous to (1 and 2), but with K substituted for Na. A mixture of Na and K was used in the source, and the mass filter was tuned for K^+. The ~ 2 eV KE shift was again obtained when the two *sodium* D lines were used, which clearly showed that excitation of K is not involved.

Discussion

The explanation of the beam deceleration has the same general basis as the well-known optogalvanic effect [9]. Sodium atoms in the source are excited. This alters the concentrations of plasma constituents. In an optogalvanic effect experiment this might be observed as an impedance reduction of the source.

We *speculate* that the following mechanism applies. The current of Na^+ from the filament is space-charge limited. This means that a sheath of Na^+ exists near the filament, and only the more energetic ions from the filament can overcome the resulting potential barrier. Laser light creates additional ionization in the sheath region, either as a result of collisional ionization of Na*, or of associative ionization [10] of two Na* to form $\text{Na}_2^+ + \text{e}^-$. This volume ionization places extra electrons within the sheath, which can result in large current amplification effects. Such effects are well known in thermionic diodes, and have been applied by Popescu and his associates [11] as sensitive ion probes in spectroscopic analyses. A reduction of the sheath potential means that less energetic ions, which have a much larger population, can reach the charge-exchange region.

Aten and Los [6] studied the relationship between the applied voltage and KE of beam atoms from a source similar to ours. They found that KE (in eV) was equal to $\Delta\Phi + \alpha V$, where $\Delta\Phi$ is the (V-independent) difference in contact potential between the filament and the charge exchange chamber. The proportionality constant α was less than the expected value of unity: it varied between 0.79 and 0.94 as a function of the distance from the filament to the grid. These distances were typical for this source. This means that difference between KE and V increases with V.

Aten and Los explained their voltage dependence by considering shielding of ions in the beam center by those at the beam edge. The ions at the center, which finally become the observed neutrals, will be reduced in speed. Their quantitative calculations were only in fair agreement with the results. However, addition of e^-, via resonant laser light, should reduce this shielding, and so their mechanism can not be used to account for our observed reduction of KE.

Our results were for our normal source operating conditions. Obvious parameters for further study might be filament temperature, filament-grid distance, Na atom density, effect of auxiliary electron sources, or effect of foreign gases.

Our proposed mechanism is *speculative*. However, our results show that a) care should be used when coaxial laser and electrically-accelerated particle beams are used, and b) analyses of particle KE could prove useful in a probe of plasma dynamics and would be complementary to the impedance monitoring used in the normal optogalvanic effect.

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