

LASER-INDUCED CHARGE TRANSFER UNDER CROSSED-BEAM CONDITIONS: APPLICATION TO THE $\text{Na} + \text{I}_2 \rightarrow \text{Na}^+ + \text{I}_2^-$ SYSTEM

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A crossed-beam charge transfer study was carried out for the $\text{Na}(3^2\text{P}_{3/2, 1/2}) + \text{I}_2 \rightarrow \text{Na}^+ + \text{I}_2^-$ system using laser excitation of the Na atom. The excitation functions were measured for the title reaction, searching for spin orbit effects. A common energy threshold of $E_0 \approx 0.23$ eV was found for both processes. In addition, similar post-threshold laws for each spin-orbit state indicate the absence of such effects over the low collision energy range.

INTRODUCTION

Charge transfer and chemi-ionization processes are well known phenomena from which valuable information about collision and reaction dynamics can be obtained.¹⁻⁸ Indeed, charge transfer thresholds, obtained either by beam-gas or beam-beam studies, provide an excellent method to estimate molecular electron affinities.¹⁻³ Nevertheless, most of these studies have been restricted to alkali metals,¹⁻³ alkaline earth atoms⁴⁻⁶ or electronically excited inert gas atoms collisions with halogen-containing molecules,^{7,8} where the threshold was surmounted by translational excitation of the reagents.

Recently, collisional ionization of oriented CF_3I and CH_3I molecules by fast K atoms has also been studied.⁹ It was found that ionization is favoured for both molecules when the atom is incident at the I end of the molecule and that this effect is most pronounced near threshold.

In the present paper we report on one experiment where a charge transfer process is studied by the crossed-beam technique, using laser excitation of the reagents to populate the ^2P states of the Na attacking atom. To our knowledge, it is one of the first studies of energy threshold determination for a charge transfer process using the laser excited atoms in their different spin-orbit states. The study was carried out for the $\text{Na}(3^3\text{P}_{3/2, 1/2}) + \text{I}_2 \rightarrow \text{Na}^+ + \text{I}_2^-$ system as described below.

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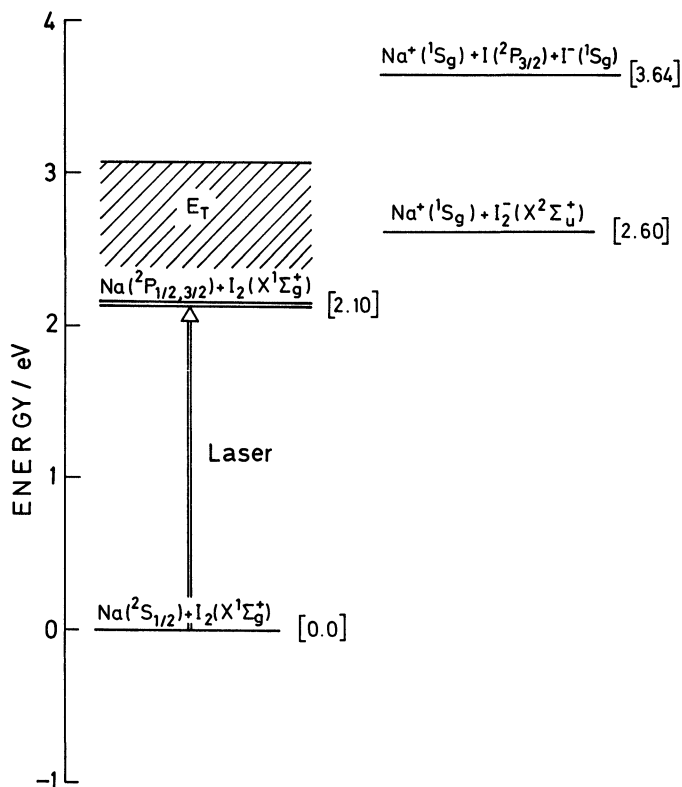


Figure 1 Energy diagram for the Na + I₂ system. Energy units in eV.

ENERGETICS

Figure 1 displays the energetic diagram for the $\text{Na} + \text{I}_2 \rightarrow \text{Na}^+ + \text{I}_2^-$ process where numbers in brackets indicate the energy of the corresponding state. Essentially, this process is endothermic in 2.59 ± 0.10 eV. This endothermicity typically has been surmounted by translational excitation of the reagents.¹⁻³ One of the main goals of the present work is to use electronic excitation by pumping the sodium atom into its two spin-orbit states, as indicated in the figure. Since the electronic excitation only accounts for 2.10 eV, the energy still required to overcome the barrier is given to the system as collision energy. Therefore, electronic versus translational energy selectivity as well as spin-orbit effects can be studied for the present charge-transfer reaction.

EXPERIMENTAL

Figure 2 shows a schematic view of the experimental arrangement. The molecular beam apparatus has been described elsewhere,^{10,11} so only a brief description is given

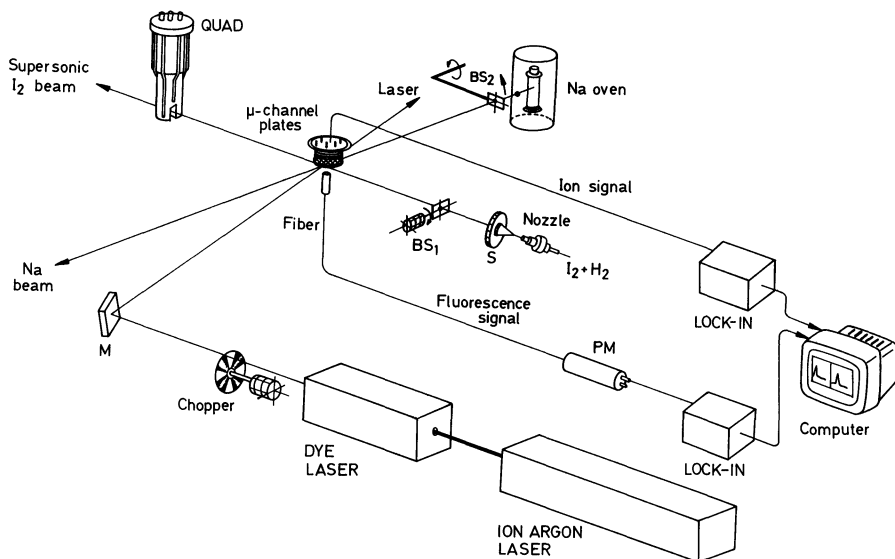


Figure 2 Schematic view of the experimental set up.

here. The I₂ beam was formed by supersonic expansion using H₂ or He as carriers. A modified (cw or pulsed) Bosch injector (90 μm hole diameter) was used as nozzle source. The I₂ beam, after being skimmed, enters the scattering chamber where it is collimated before being crossed at 90° with the Na beam. I₂ beam densities and velocity distributions were determined by a quadrupole mass filter and time-of-flight technique. The Na beam is formed in a hot oven using a stainless steel pipe as crucible. The oven details and characterization have been reported elsewhere,¹¹ so their description is omitted for brevity. The sodium beam is measured and characterized by time-of-flight technique using a Re surface ionization detector^{10,12} and/or measurement of the laser induced fluorescence by means of an optical fibre and a photomultiplier. Care was taken to avoid Na₂ formation by continuously checking the absence of chemi-ionization signal from the Na₂ + I₂ reaction. Since the energy threshold for the ground state reaction Na + I₂ → Na⁺ + I₂⁻ is well known to be $E_{th} \approx 2.6 \pm 0.1$ eV,^{1,2} all the runs for the present work were carried out at lower collision energies to guarantee no contribution to the ion signal from the ground state reaction.

The ion signal was collected using a home-made ion detector allocated right above the scattering center. The detector is made of two microchannel plates (Comstock CP-602). Gain factors of 10⁵ or higher were observed with respect to simple Faraday cup detection.

As it is well known, to prepare a significant population of excited Na atoms is not a trivial problem because of its hyperfine structure.^{13a} For the present work, we used a linear dye laser (Coherent 599-01) in multimode pumped by an argon ion laser (Coherent Innova-90). The dye laser used Rhodamine 6G that provides a tuning range from 570 nm to 630 nm. The tuning is realized by rotating an intracavity tilted

3-plate birefringent filter by means of a continuously running dc motor that is supplied by a pulse width modulating regulator. The laser wavelength can be read out from a micrometer screw with an accuracy of 0.1 nm. This micrometer screw is calibrated using the optogalvanic effect in a hollow cathode lamp. For the experiments, the laser beam was mechanically modulated at 75 Hz. The measured linewidth and power of the dye laser were 13.3 GHz and 80 mW, respectively. For all the runs, the laser was perpendicularly polarized to the plane of the beams and so to the relative velocity vector.

Data collection consisted of both laser induced fluorescence of the Na beam and charge transfer signal from $\text{Na}^* + \text{I}_2 \rightarrow \text{Na}^+ + \text{I}_2^-$ collisions as a function of the laser wavelength which was continuously varied over the 5889–5897 Å spectral range to cover both $\text{Na}(3^2\text{S}_{3/2})$ and $\text{Na}(3^2\text{S}_{1/2} \rightarrow 3^2\text{P}_{1/2})$ transitions. The laser induced fluorescence and charge transfer spectra were corrected by subtracting the background with the Na and I_2 beams off.

In addition, during all the runs, the Na beam intensity was maintained constant and the fluorescence intensity ratio of the two $^2\text{P}_{3/2} \leftarrow ^2\text{S}_{1/2}$ and $^2\text{P}_{1/2} \leftarrow ^2\text{S}_{1/2}$ lines was found to be $I_{3/2}/I_{1/2} = 2.0 \pm 0.2$, i.e. in good agreement with the expected 2:1 ratio. As a result, we assume that optical thickness and saturation effects,^{13b} if present, were similar for the two spin-orbit components and consequently they did not affect the spin-orbit normalization of the charge transfer cross-section data.

Once several spectral runs were taken, the whole procedure was repeated changing the relative velocity by varying the nozzle carrier pressure maintaining the Na beam fixed.

Data acquisition was interfaced to an INVES AT computer for storage and further analysis. As mentioned before, our aim was to measure both $\text{Na}(3^2\text{P}_{3/2,1/2}) + \text{I}_2 \rightarrow \text{Na}^+ + \text{I}_2^-$ charge transfer excitation functions to obtain information on the collision dynamics, spin-orbit and threshold effects of the charge transfer.

Table 1 lists all the relevant experimental parameters and conditions of the present work.

Table 1 Typical experimental conditions

| | |
|--|-------------|
| <i>Beams</i> | |
| Na oven temperature/K | 1025 |
| Nozzle oven temperature/K | 300 |
| Na beam divergence/degrees | 1 |
| I_2 beam divergence/degrees | 0.9 |
| Collision energy range/eV | 0.30–0.70 |
| Typical Na velocity/ m s^{-1} | 1050 |
| Typical I_2 velocity/ m s^{-1} | 2100 |
| Pressure in the scattering chamber/mbar | 1.10^{-6} |
| <i>Detectors</i> | |
| Microchannel plates HV/V | –2000 |
| Ion repeller/V | +100 |
| Photomultiplier HV/V | 500 |
| <i>Laser</i> | |
| Linewidth/GHz | 13, 3 |
| Power/mW | 80 |

RESULT AND DISCUSSION

Beams Characterization

As usual, the I₂ densities and most probable beam velocities were determined as a function of the I₂ mole fraction in H₂/I₂ mixtures. These measurements were carried out by using quadrupole mass spectrometry and time-of-flight (TOF) techniques. Typical experimental values of I₂ densities and velocity distributions are displayed in Figures 3 and 4. The reader is addressed to ^{10,12} for more details about these methods.

Figure 5 shows a time-of-flight spectrum of the laser induced fluorescence of the Na beam, corresponding to the ²P_{3/2} ← ²S_{1/2} transition at 5889 Å. This experimental time-of-flight distribution was fitted to:

$$f(v) = N \left(\frac{v}{\alpha_s} \right)^2 \exp \left[- \left(\frac{v_s - v}{\alpha_s} \right)^2 \right] \quad (1)$$

after the proper convolution over the known broadening effects (gate, RC, etc.). v_s is the most probable velocity and α_s is the width parameter $\alpha_s = (2kT_s/m)^{1/2}$, T_s being the translational temperature of the beam.

The same procedure was used to analyze the time-of-flight of the I₂ beams. Typical v_s values of both Na and I₂ beams are also displayed in *Table 1*.

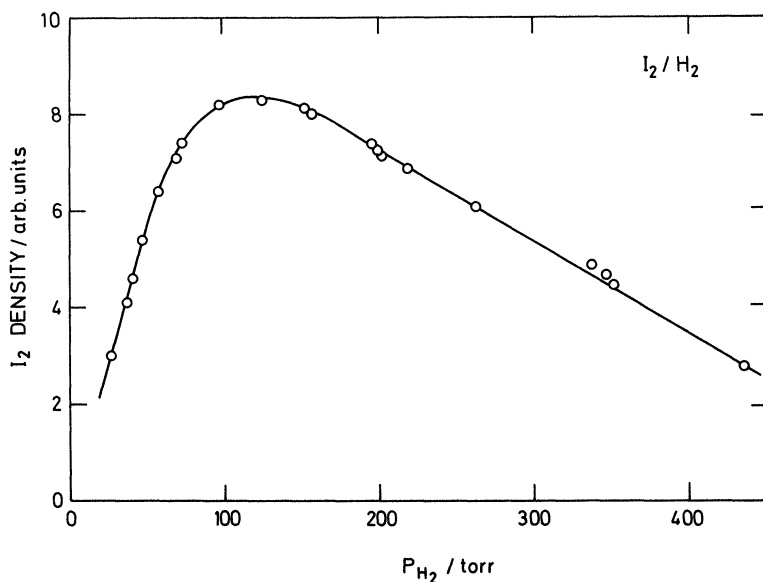


Figure 3 I₂ density in relative units as a function of the H₂ (carrier) pressure in the nozzle oven, obtained by quadrupole mass analysis of the seeded beams.

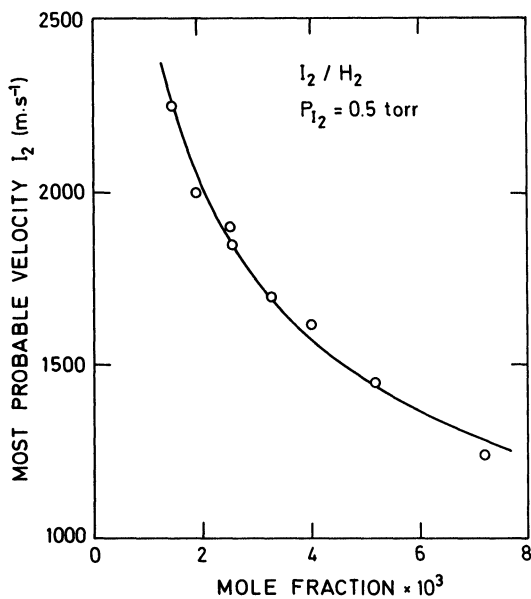


Figure 4 Most probable I_2 beam velocities as a function of I_2/H_2 mole fraction.

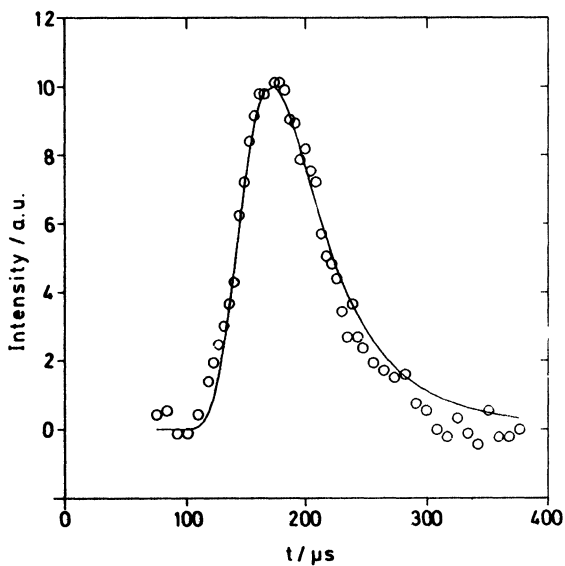


Figure 5 Time-of-flight spectrum of the laser induced fluorescence of the Na beam corresponding to the $^2P_{3/2} \leftarrow ^2S_{1/2}$ atomic transitions (see text for details).

Charge Transfer Spectra and Excitation Functions

Figure 6 shows typical laser induced charge transfer spectra, i.e. positive ion signal versus laser wavelength from the crossed-beam Na* + I₂ → Na* + I₂⁻ collisions. These spectra are normalized with both Na* and I₂ densities. Note that at the indicated collision energies, all but no spin-orbit effect is observed in the charge transfer signal.

Figure 7 shows the two spin-orbit charge transfer excitation functions over the near-threshold collision energy range. These functions were obtained using the following equation:¹⁴

$$\sigma_R = \frac{F_{\text{ion}}}{n_{\text{Na}^*} n_{\text{I}_2} \Delta V v_R}, \quad (2)$$

where ΔV is the cross-beam volume, held constant during all the experiments. F_{ion} is the total ion flux and n_{Na^*} and n_{I_2} are both beam densities. v_R is the relative velocity of the reagents. Solid line represents the best data fit to the threshold law¹⁴

$$\sigma_R = A \frac{(E_T - E_0)^n}{E_T} \quad (3)$$

with $n = 2.5$ and $E_0 = 0.35$ eV as the best fitted parameters.

Charge transfer threshold for the ground charge transfer process is known to be E_0 (ground Na) = 2.6 eV.^{1,2} Therefore, our value of 0.35 eV is in good agreement with it, considering that the electronic excitation due to the Na($3^2P_{1/2,3/2}$) states, $E^* \simeq 2.1$ eV is used to promote the charge transfer and indicating the absence of any electronic versus translational selectivity for this atom-molecule charge transfer processes.

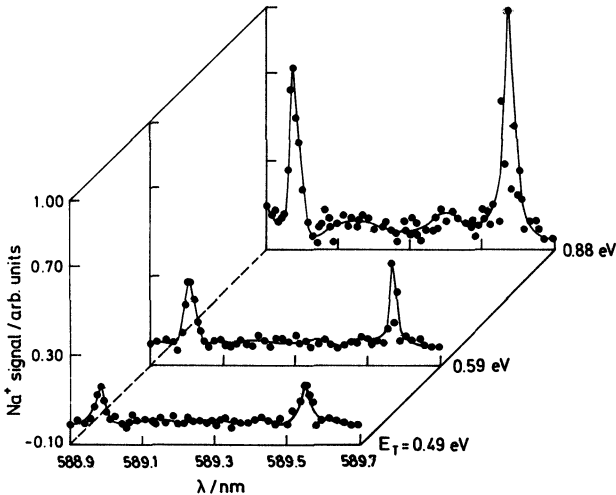


Figure 6 Na⁺ ion yield as a function of laser wavelength and collision energy.

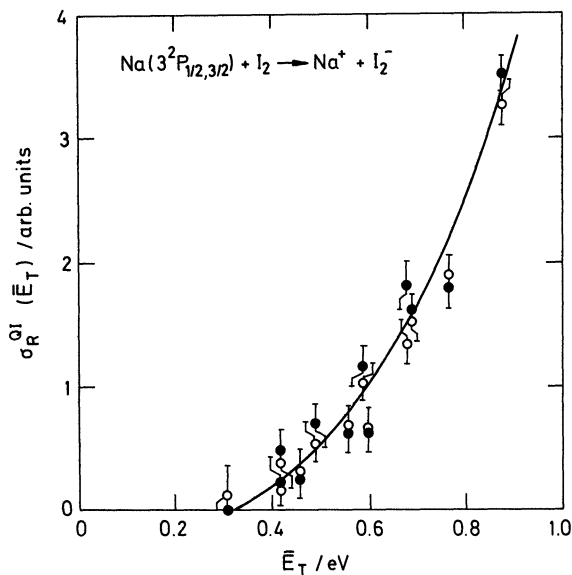


Figure 7 Excitation function for the laser induced charge transfer processes $\text{Na}(3^2P_{3/2,1/2}) + \text{I}_2 \rightarrow \text{Na}^+ + \text{I}_2^-$. Open cycles: $\text{Na}(^2P_{1/2})$. Solid line: best fit using equation (2) of the text with $n = 2.5$ and $E_0 = 0.35 \text{ eV}$. This convolution was made taking into consideration the velocity spread of both beams.

We can now determine the I_2 molecule electron affinity from this threshold measurements as

$$EA(\text{I}_2) = IP(\text{Na}) - E^* - E_0 = 5.15 - 2.10 - 0.35 = 2.69 \text{ eV},$$

where $IP(\text{Na})$ is the ionization potential of the Na atom and E^* and E_0 stand for the electronic energy of the $^2P_{3/2}$ state and the threshold energy, respectively.

This value approaches the one that was previously determined by Los and co-workers^{1,2} from the ground-state process ($2.55 \pm 0.05 \text{ eV}$) although the difference between these two values:

$$EA_{\text{I}_2}(\text{present result}) - EA_{\text{I}_2}(\text{previous result}) = 2.69 - 2.55 = 0.14 \text{ eV},$$

is slightly higher than our uncertainty in the energy threshold $\Delta E_0 = 0.05 \text{ eV}$. Some possible factors that could explain this difference may be:

- (i) The use of electronically (instead of translationally) excited Na atoms for the present study. This may produce an enhancement of the I_2 vibrationally excited and therefore an increase of the vertical electron affinity, since the I_2^- equilibrium distance is greater than that of I_2 (see reference 2).
- (ii) The present excitation function was fitted using equation (2), changing simultaneously the two E_0 and n parameters. In the previous studies,^{1,2} a fixed value of n (typically $n = 1$, i.e. linear functionality) was *a priori* assumed to obtain the best (fitted) value of E_0 .

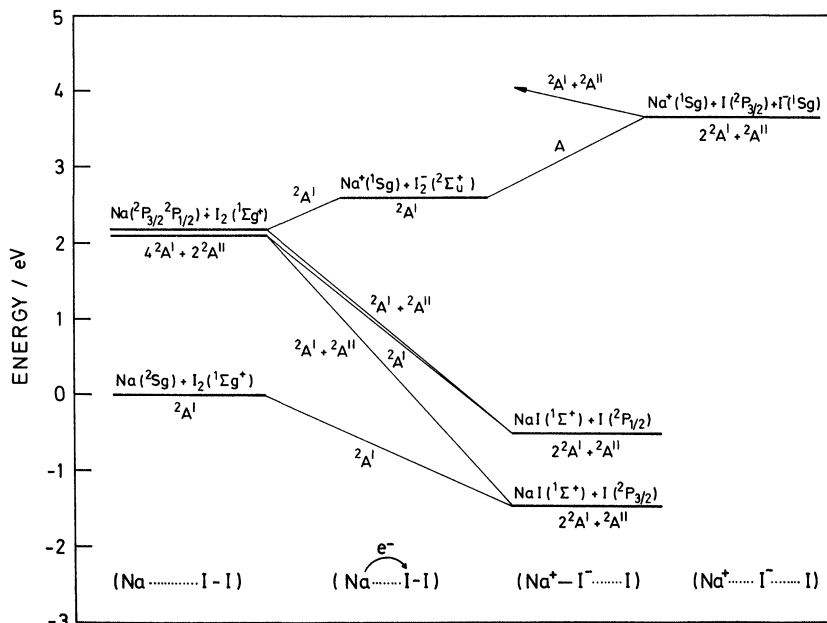


Figure 8 Adiabatic correlation between the Na + I₂ reactants and the Na⁺ + I₂⁻ products using the C_s group of symmetry.

(iii) The combined use of both electronic and translational excitation in the present study makes the total energy uncertainty lower than in the previously reported studies^{1,2} where only translational excitation was used.

Although important spin-orbit effects have been found in reactive and non-reactive collisions,⁶ it is interesting to point out the absence of any significant spin-orbit effect in the charge transfer process. Figure 8 shows the adiabatic correlation of the Na + I₂ system using the C_s group of symmetry. From an adiabatic correlation point of view, only the Na(2P_{3/2}) + I₂(¹Σ_g⁺) reaction correlates with the charge transfer Na⁺ + I₂⁻ products, but in the present work, the lack of such effect is not surprising. Because of the very small fine-structure splitting in the Na atom case (ΔE = 2 meV), non-adiabatic mixing in the entrance channel may probably scramble the incident spin-orbit levels, leading to the same post-threshold law as it was found.

Work is in progress to extend the present study to higher collision energies as well as to study alignment (of P orbital) effects in the charge transfer cross-section.

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