Strong Alignment Effect in Quasiresonant Charge Transfer between Laser-Excited Sodium Atoms and C_{60}

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We observe a strong alignment effect ($\langle \rho_{\sigma\sigma} \rangle = 0.8 \pm 0.2$) in quasiresonant charge transfer collisions between Na($3p$) and C_{60} at thermal energies. This implies that practically only excited sodium atoms with their electronic charge cloud asymptotically aligned along the relative velocity vector lead to charge transfer. This is interpreted as being due to a combination of "orbital locking" and the strong π-like character of the fullerene lowest unoccupied molecular orbital. [S0031-9007(99)08901-2]

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Experimental and theoretical investigations of electronic outer shell alignment and orientation effects in atomic collisions have provided a wealth of detailed information on the dynamics of the collisions. Systematic studies on a few model systems have led to the development of relatively simple, intuitive "hand-waving" pictures of what happens to the electrons during the course of the encounter [1,2]. The main motivation for the difficult and time-consuming experimental studies has, however, been to provide stringent and very detailed tests for sophisticated theoretical models [2]. These theories may then, in turn, be used with confidence to compute parameters of practical interest for systems that are experimentally inaccessible. A comprehensive database of all atomic cross sections that are of practical importance, e.g., for plasma surface etching of semiconductor devices or fusion plasmas cannot be derived purely from experimental sources.

There have been some attempts to extend experimental electronic alignment and orientation studies to collisions with diatomic molecules [3–6]. In most cases the results show only a small alignment effect and are rather difficult to interpret due, first, to the higher complexity of the collision systems but also to the random orientation of the molecule with respect to the relative velocity vector of the collisions. Theoretical treatments are also more challenging in molecular collision systems due to the increased number of degrees of freedom, and it is only recently that general methods have been developed which are powerful enough to treat such systems [7,8].

In this Letter we report experiments using a complex molecular target where the problem of the relative orientation of the molecule does not, to a first approximation, play a role. The very high molecular symmetry of C_{60} (I_h) combined with the delocalized nature of the electronic structure make it an ideal model system for extending atomic alignment and orientation techniques to complex molecular systems.

As a first system, we have chosen to study the effect of charge cloud alignment in scattering-angle-averaged thermal charge transfer collisions,

$$\mathrm{Na}(3p) + \mathrm{C_{60}} \rightarrow \mathrm{Na^+} + \mathrm{C_{60}^-}. \qquad (1)$$

Although such experiments with cylindrical symmetry cannot give the full range of dynamical details available from experiments with planar symmetry, they probe the net alignment effect averaged over all impact parameters and thus the contribution most important for the total collision process. This is particularly so for large impact-parameter charge transfer collisions. The results of such studies can provide a great deal of insight into the collision mechanisms [2]. As well as providing an excellent model system for studying charge transfer in complex systems, alkali atom–fullerene charge transfer is also of considerable fundamental interest due to its relevance for high temperature superconductivity in alkali metal intercalated fullerides.

A schematic diagram of the apparatus used is shown in Fig. 1. The sodium beam emerges from an oven at a temperature of typically 460 °C with a separately heated nozzle with an aperture of 0.1 mm. The beam is operated

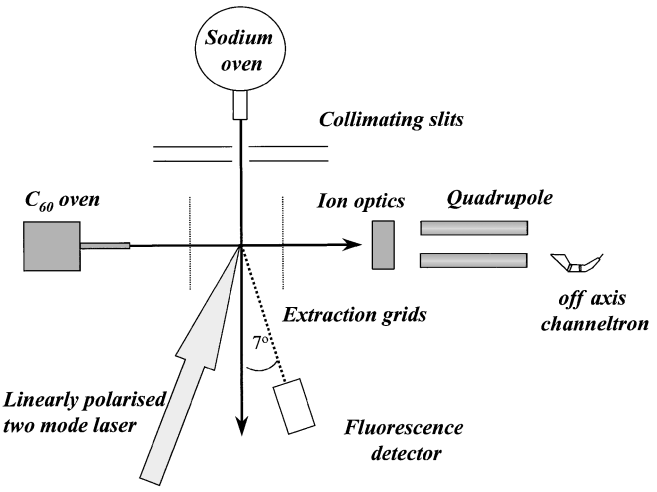

FIG. 1. Schematic diagram of the apparatus.

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under conditions typically between effusive and jet-type with an average velocity of approximately 1200 m s^{-1}. It is collimated using a liquid nitrogen cooled copper aperture and a heated steel slit to produce a target 5 mm wide by 2 mm high in the interaction region. The fullerene beam, at right angles to the Na beam, is produced from an oven heated to 500 °C with a nozzle consisting of a 15 mm long tube with an inner diameter of 1.5 mm. This produces a highly directional beam with an average velocity of 150 m s^{-1}. The relative velocity vector ($\mathbf{v}_{\mathrm{rel}}$) for these collisions thus lies close to the direction of the Na atom beam. The sodium atoms are optically pumped to the $\mathrm{Na}(3^2P_{3/2}, F = 3, M_F)$ states in the interaction region by a linearly polarized two-mode cw dye laser propagating at right angles to both the atom and the fullerene beams. The laser is focused to a spot size of about 1 mm. The use of two-mode excitation (excitation from both the hyperfine levels of the ground electronic state) leads to approximately 40% excited atoms in the interaction region compared to about 8% using single-mode excitation due to the loss of atoms from the pump cycle [9]. The alignment of the excited sodium atoms was monitored by detecting the fluorescence signal with a photodiode placed in the collision plane at an angle of 7° with respect to the sodium beam direction (Fig. 1). The interaction region was shielded from magnetic fields by μ metal. Charge transfer was detected by extracting the negatively charged fullerenes with a constant electric field of 140 V/cm applied across the interaction region, and detecting them in a differentially pumped quadrupole mass spectrometer. The mass spectrometer was used in "single-ion" mode, i.e., it was tuned to allow only ions of $m/q = 720$ to be detected. The polarization direction of the laser light was rotated continuously by a polarization rotator driven by a stepper motor at a speed of 24 degrees per second. The fluorescence intensity from the excited atoms and the charge transfer signal were simultaneously registered with a digital oscilloscope. No charge transfer signal was observed without the presence of both the sodium beam and the laser. The process that we are investigating is quasiresonant. The ionization potential of $\mathrm{Na}(3p)$ is 3 eV which should be compared with the C_{60} electron affinity of 2.65 eV [10]. The remaining energy difference can be compensated for by the high vibrational excitation of the fullerene at the beam temperature of 500 °C.

Figure 2 shows the experimentally determined dependence of the C_{60}^- intensity on the polarization direction of the laser light. From this data it is possible to extract the integral alignment parameter $\langle \rho_{\sigma\sigma} \rangle$ [2],

$$\langle \rho_{\sigma\sigma} \rangle = \frac{\sigma_\sigma}{\sigma_\sigma + \sigma_{\pi^+} + \sigma_{\pi^-}}, \tag{2}$$

where σ_σ, σ_{π^+}, and σ_{π^-} are the relative cross sections for charge transfer from atomic σ (aligned along $\mathbf{v}_{\mathrm{rel}}$), π^+ (perpendicular to $\mathbf{v}_{\mathrm{rel}}$, in the scattering plane), and π^- (perpendicular to the scattering plane) orbitals, respectively. The method used for data analysis is briefly sketched here; more details can be found in [2,9]. The scattering intensity for experiments with cylindrical symmetry is given by

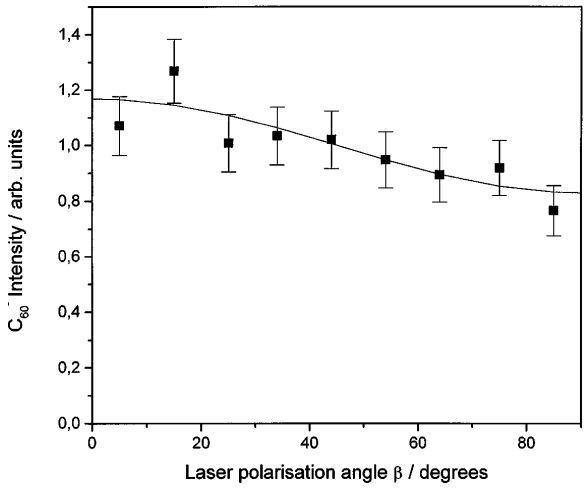

FIG. 2. Dependence of the C_{60}^- ion signal from thermal $\mathrm{Na}(3p) + C_{60}$ collisions on the polarization direction β, with respect to the relative velocity vector, of the laser light used to excite the sodium atoms. The full line is a fit to the experimental data: $1 + 0.17\cos(2\beta)$.

$$I(\beta) = \frac{1}{3}(\sigma_\sigma + \sigma_{\pi^+} + \sigma_{\pi^-})(1 + g_2 S_{20}) - g_2 S_{20}\left[\sigma_\sigma \cos^2\beta + \frac{1}{2}(\sigma_{\pi^+} + \sigma_{\pi^-})\sin^2\beta\right], \tag{3}$$

where β is the angle of the laser polarization vector with respect to $\mathbf{v}_{\mathrm{rel}}$, g_2 is a numerical factor [$= \frac{1}{2}$ for $\mathrm{Na}(3^2P_{3/2})$], and S_{20} is the optically prepared multipole moment in the L frame of reference. $\langle \rho_{\sigma\sigma} \rangle$ can thus be written in terms of the asymmetry of the charge transfer signal,

$$P_{\mathrm{ion}} = \frac{I(0°) - I(90°)}{I(0°) + I(90°)} \tag{4}$$

as follows

$$\langle \rho_{\sigma\sigma} \rangle = \frac{1}{3} - \frac{4P_{\mathrm{ion}}}{3g_2 S_{20}(3 - P_{\mathrm{ion}})}. \tag{5}$$

The optically prepared multipole moment, S_{20}, is obtained from the dependence of the fluorescence signal on the laser polarization angle. The method by which this is done was described in detail by Fischer and Hertel [11]. The experimental fluorescence dependence is shown in Fig. 3. In this case it is generally more convenient to give the polarization angle of the laser light with respect to the detection plane [11], however, in our particular geometry the detection plane coincides with the direction

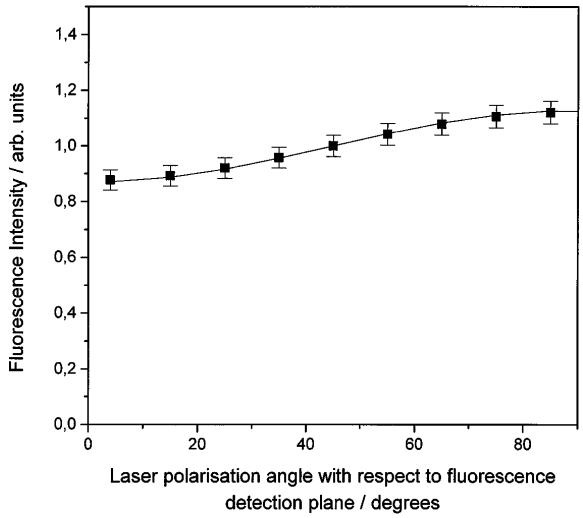

FIG. 3. Dependence of the fluorescence from Na($3p$) on the polarization direction β, with respect to the fluorescence detection plane, of the laser light used to excite the sodium atoms. The full line is a fit to the experimental data: $1 - 0.13\cos(2\beta)$.

of $\mathbf{v}_{\mathrm{rel}}$. The optically prepared multipole moment for the particular case of relevance here is given by

$$S_{20}(L) = \frac{8P_L}{(3 - P_L)}, \tag{6}$$

where P_L, the asymmetry of the fluorescence intensity, is given by an expression analogous to Eq. (4).

In our experiments (Fig. 3) $P_L = -0.13 \pm 0.01$ giving a value of S_{20} of -0.33 ± 0.03. This is considerably less than the theoretical maximum value of -0.67 [11]. The main reason for the greater degree of depolarization in our experiments, compared to the normal depolarization due to fine- and hyperfine coupling in the sodium atom, is the presence of the electrical field used to extract the negative fullerene ions from the interaction region [12].

Inserting this value into Eq. (5) along with the measured asymmetry of the charge transfer signal ($P_{\mathrm{ion}} = 0.17 \pm 0.05$) gives $\langle \rho_{\sigma\sigma} \rangle = 0.8 \pm 0.2$. This is a surprisingly large alignment effect and means that the asymptotic preparation of an atomic σ state is 8 times more likely to lead to charge transfer with C_{60} than the asymptotic preparation of π states.

A simple intuitive model developed for ion-atom collisions [2,13] can describe what may be happening in these low-energy collisions where an adiabatic or quasimolecular picture of the collision is appropriate (i.e., where the collision partners can be regarded as forming a quasimolecule during the collision). In this situation orbital following has been shown to be a reasonable approximation for simple collision systems. This term, coined by Rettner and Zare [4], refers to a dynamical behavior in which the atomic electron charge cloud is fixed to the internuclear axis during the collision process. Since the molecular axis rotates during the collision (impact parameter $b > 0$), this

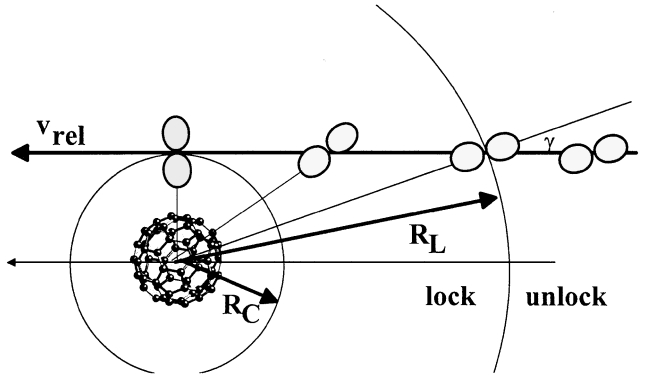

FIG. 4. Schematic illustration of the orbital following the model used to explain the large alignment effect observed experimentally. The atomic orbital, asymptotically prepared as a σ state (aligned along the relative velocity vector) "locks in" to the internuclear axis at a large distance R_L from the C_{60}. It then rotates during the collision so that a maximum overlap with the π-like LUMO of the fullerene is assured on a charge transfer at the distance R_C.

implies that the charge cloud also rotates with respect to a space-fixed frame. The optimum alignment angle of the atomic charge cloud for the particular reaction will depend on the distance, R_L, at which the collision partners "lock" to one another. Beyond this distance the atomic orbital will tend to stay space fixed. A schematic diagram of this situation is shown in Fig. 4. This obviously is a highly simplified picture but it does help to make the experimental results intuitively plausible.

Charge transfer will occur to the lowest unoccupied molecular orbital (LUMO) of C_{60}. It is known that the molecular orbitals that lie energetically in the region of the highest occupied–lowest unoccupied molecular orbital (HOMO-LUMO) gap have a strong π-character [14,15]. There will thus be a good overlap of the atomic and fullerene orbitals when the atomic charge cloud is aligned as shown in the figure leading to a high probability of charge transfer.

The effect that we observe is really exceptionally high for such a complex molecular collision system. Although the simple model that we present here is intuitively attractive it should be confirmed by detailed theoretical calculations. This is certainly a very challenging theoretical task but we hope that the very clear experimental results we have presented here will encourage this work to be done.

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