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Alignment of molecules by strong laser pulses

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Abstract. We review how moderately intense laser fields offer an approach to alignment of molecules [1]. In particular, molecules can be aligned along a given space fixed axis, forced to a plane, or their rotations about all three possible axes can be eliminated by choosing a linearly polarized, a circularly polarized, or an elliptically polarized alignment field, respectively. We show how molecules in the gas phase can be aligned by turning on the laser field either slowly (a few nanoseconds) or fast (a few picoseconds) with respect to the rotational period of the molecules. The role of the intensity of the laser field and the rotational temperature of the molecules is discussed. Before concluding we describe how aligned molecules enables control and selectivity in the interaction between polarized light and molecules.

PACS. 33.15.Bh General molecular conformation and symmetry; stereochemistry – 32.80.Lg Mechanical effects of light on atoms, molecules, and ions – 33.80.Gj Diffuse spectra; predissociation, photodissociation – 33.80.Rv Multiphoton ionization and excitation to highly excited states (e.g. Rydberg states) – 34.50.Lf Chemical reactions, energy disposal, and angular distribution, as studied by atomic and molecular beams

1 Introduction

From a chemical point of view alignment or even orientation is important because most chemical reactivity depends on the relative orientation of the reactants. In this connection, alignment refers to order of the molecules with respect to given axes fixed in space. If, in addition, the molecules also have a preferred direction with respect to the space fixed axes, *i.e.* the inversion symmetry is broken, they are said to be oriented. We use 1-D alignment to describe alignment with respect to one space fixed axis. Similarly, 2-D and 3-D alignment refers to alignment of the molecular geometry with respect to a space fixed 2-dimensional (3-dimensional) coordinate system. In this paper we will only discuss alignment

As an example of a bimolecular reaction where alignment is important we mention the reaction between an alkali atom, such as sodium, and an ozone molecule producing sodium oxide and molecular oxygen. Symmetry considerations of the electronic orbitals involved in the reaction indicates that the rate is much higher if the Na atom attacks O_3 perpendicular to the plane rather than parallel to the plane [2]. In this case 2-D alignment of the O_3 would therefore be necessary to control or study the steric effects. Molecular alignment is also important for reactions induced through absorption of polarized light due to the symmetry selection rules [3]. A simple example is vibrational excitation of CO_2: excitation of the fundamental asymmetric stretch vibration is maximized if the exciting light is polarized along the molecular axis, whereas excitation of the fundamental bending vibration is maximized if the exciting light is polarized perpendicular to the molecular axis.

2 Observation of alignment

2.1 1-dimensional adiabatic alignment

The most simple form of alignment is that produced by a CW field [4–6]. In this case the eigenstates of the rotational part of the Hamiltonian are the so-called pendular states [7]. Each pendular state is a superposition of field free rotational states (spherical harmonics, in the case of a diatomic molecule) locked together coherently due to the presence of the strong alignment field. Experimentally, it is necessary to turn on the alignment field, which is accomplished through the use of intense laser pulses. If the rise time of the pulse is longer than the rotational period of the molecules, the molecules will evolve adiabatically from field free rotational states into pendular states. Since the rotational period, $1/2Bc$, B being the rotational constant, is less than a nanosecond for most small molecules (fewer than 10 atoms) the application of ns pulses from commercial available ns lasers (typical pulse duration 3–15 ns) should be sufficient to ensure adiabatic conditions.

The next issue is how to measure molecular alignment. One approach is to perform rotational spectroscopy since

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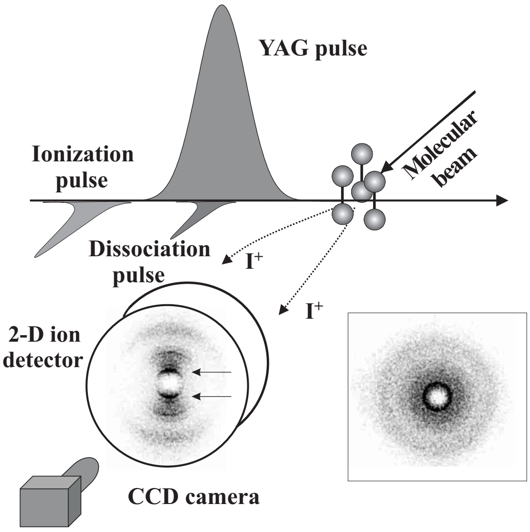

Fig. 1. Schematic of the experimental setup. The I^+ image on the detector (in the inset) is obtained when the YAG pulse is present (absent).

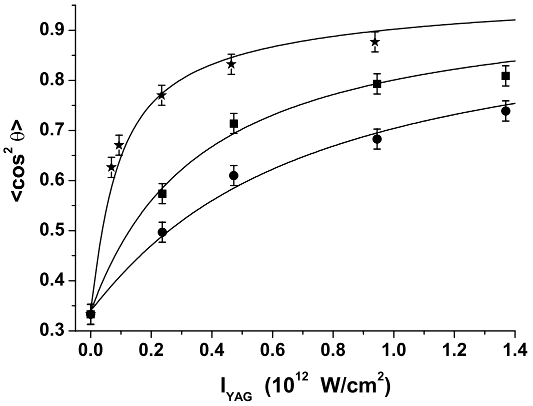

Fig. 2. $\langle\cos^2\theta\rangle$ as a function of I_{YAG} for three different rotational temperatures. Circles: $T_{\mathrm{rot}} = 7$ K, squares: $T_{\mathrm{rot}} = 3.5$ K, stars: $T_{\mathrm{rot}} = 1$ K.

the rotational states are significantly shifted by the strong alignment field. This approach was taken by Felker *et al.* who performed stimulated Raman spectroscopy on the pendular states of napthalene trimers [8]. Using the frequency doubled output (532 nm) from a ns Nd:YAG laser as both the alignment field and one of the Raman fields Felker *et al.* carried out the first unambiguous observation of laser induced alignment.

An alternative approach is to use photodissociation as a probe because the direction in which the photofragments are emitted carries information on the spatial orientation of the molecule at the time of dissociation [9]. In Figure 1 we show a diagram of our experimental setup used to create and detect alignment. A rotationally cold molecular beam is crossed at 90° by three pulsed laser beams. The almost transform limited alignment pulses are 3.5 ns long and originate from a Nd:YAG laser. Using its fundamental wavelength ensures nonresonant alignment since most molecules do not absorb at 1064 nm. In the first adiabatic alignment experiment I_2 molecules were studied. They were dissociated by a 100-fs-long pulse ($\lambda = 688$ nm), synchronized to the peak of the YAG pulse, and the photofragments were ionized by a second, intense, 100-fs long pulse ($\lambda = 800$ nm), delayed 200 ps with respect to the dissociation pulse. A weak static field pushed the I^+ ions towards a 2-dimensional ion detector allowing the measurement of their angular distribution. The I^+ image shown on the detector is recorded when a 5×10^{11} W/cm^2 YAG pulse, polarized vertically, is applied. The arrows mark the I^+ ions originating from ionization of the photofragments. The pronounced angular localization of the photofragment ions shows that the molecules are being aligned along the YAG polarization. Without the YAG pulse, the I^+ image is circularly symmetric as shown in the inset.

For a given molecule the degree of alignment is determined by the alignment field strength and the rotational temperature (T_{rot}). This is illustrated in Figure 2 where the degree of alignment, $\langle\cos^2\theta\rangle$, is plotted *versus* the YAG intensity (I_{YAG}) for three different rotational temperatures (θ is the polar angle between the YAG polarization and the molecular axis). The $\langle\cos^2\theta\rangle$ values shown in Figure 2 are obtained from 2-D ion images similar to those illustrated in Figure 1. As expected [6] $\langle\cos^2\theta\rangle$ increases with increasing I_{YAG} and with decreasing T_{rot}. Figure 2 shows that T_{rot} is an efficient control parameter for the degree of alignment: at $T_{\mathrm{rot}} = 7$ K, $I_{\mathrm{YAG}} \sim 10^{12}$ W/cm^2 is necessary to obtain $\langle\cos^2\theta\rangle = 0.7$. In comparison, at $T_{\mathrm{rot}} = 1$ K the same degree of alignment is obtained for an intensity ten times lower.

Adiabatic 1-dimensional alignment is applicable to all molecules possessing an anisotropic polarizability. We carried out experiments on a number of different molecules, in addition to I_2, and observed alignment of the linear molecules ICl, CS_2, the symmetric top molecule CH_3I, and the asymmetric top molecules C_6H_5I, C_6H_5Br, o-$C_6H_4Br_2$, *p*-$C_6H_4Br_2$, and 3,4 $C_4H_2SBr_2$ [10]. Besides the naphthalene trimers Felker *et al.* also showed that Ar-benzene complexes can be aligned [11].

2.2 3-dimensional adiabatic alignment

In the case of linear or symmetric top molecules 1-D alignment is sufficient for a complete control of the molecular geometry. By contrast, for an asymmetric top molecule exposed to a linearly polarized alignment field only the axis with the largest polarizability will be strongly angularly confined, but the molecule can rotate (almost) freely around this axis. To extend the control such that full 3-dimensional confinement becomes possible an elliptically polarized field is used [12]. In a simple picture this can be understood by considering when the polarizability interaction between the asymmetric top molecule and the field is minimized. This occurs when the most polarizable axis of the molecule is aligned along the major axis of the field and, simultaneously, the molecular axis with the second largest polarizability is aligned along the minor axis of the field. If the molecule is rigid its third axis

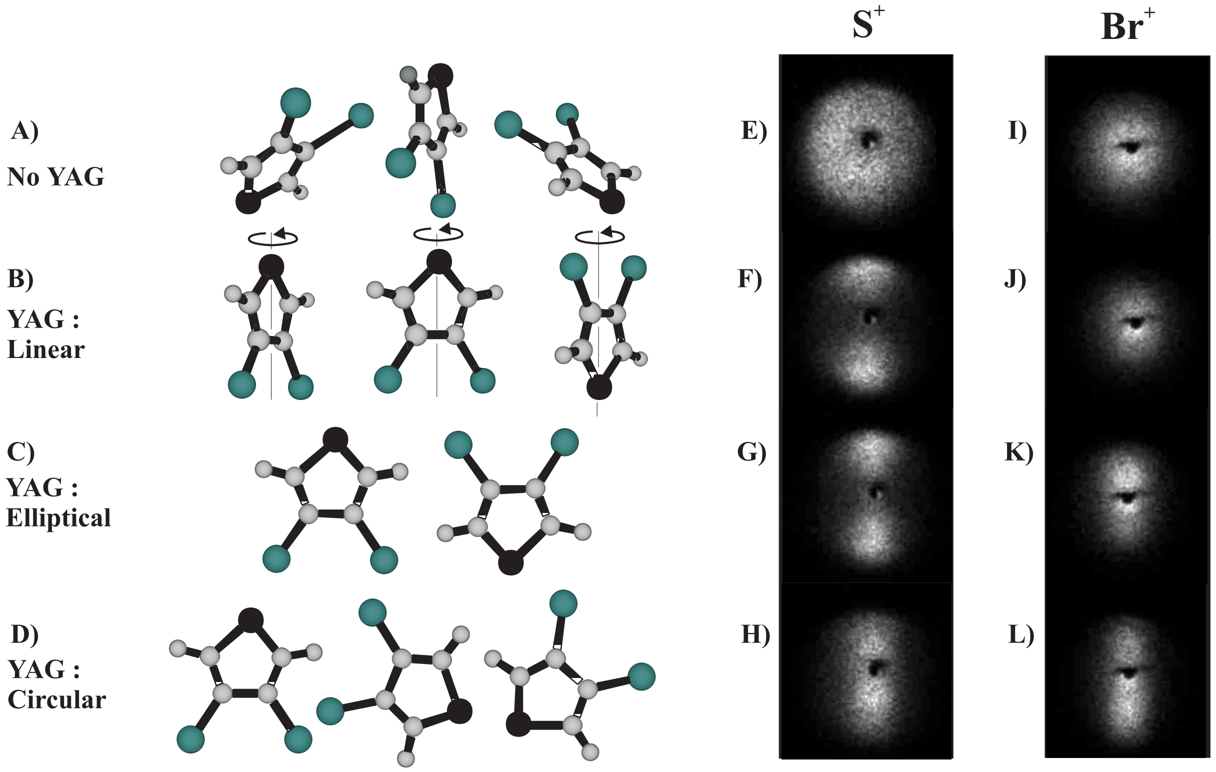

Fig. 3. Illustration of the orientational dependence of 3,4 dibromothiophene molecules for (A): no YAG field, (B): a linear YAG field, (C): an elliptically polarized YAG field, (D): a circularly polarized YAG field. (E–L) S^+ and Br^+ ion images for the different YAG polarizations. For the S^+ images the major axis is vertical and the minor axis is perpendicular to the image plane. For the Br^+ images the minor axis is vertical and the major axis is perpendicular to the image plane.

is automatically aligned perpendicular to the plane of the field. This 3-dimensional alignment as well as no alignment and 1-D alignment is illustrated in Figures 3A–3C in the case of 3,4 dibromothiophene molecules. Solution of the rotational Schrödinger equation for this molecule in an intense elliptically polarized field confirms that all three Euler angles are confined in the way predicted above [12]. Experimentally, an elliptically polarized 3.5 ns YAG pulse was used to study 3-D alignment. To measure the orientation of the molecules they were Coulomb exploded by an intense 20 fs pulse synchronized to the peak of the YAG pulse. The angular distributions of both S^+ and Br^+ ions were recorded, since, for symmetry reasons, the S^+ ions recoil along the C_2 axis of the molecule whereas the Br^+ ions are ejected in the molecular plane. In the absence of an alignment field both the S^+ and Br^+ ion images are circularly symmetric (Figs. 3E, 3I), showing that the molecules are randomly oriented. When a linearly polarized YAG field is applied, the S^+ ion image recorded with the YAG polarization parallel to the detector is angularly confined along this polarization (Fig. 3F), whereas the Br^+ ion image obtained with the YAG polarization perpendicular to the detector is circularly symmetric (Fig. 3J). These two observations show that the C_2 axis (the symmetry axis) is aligned along the YAG polarization. When the YAG pulse is made elliptically polarized, the circular symmetry of the Br^+ ion image is broken and instead the ions become localized along the minor axis of the YAG field (Fig. 3K). Since the S^+ ions remains confined along the major axis (Fig. 3G) we conclude that the plane of the 3,4 dibromothiophene molecules is aligned to the YAG polarization plane and the C_2 axis is confined along the major axis. This is 3-dimensional alignment. Increasing the ellipticity we observe that the molecular plane becomes more aligned whereas the C_2 axis becomes less confined. In the limit of circular polarization the molecular plane is strongly aligned to the polarization plane but the molecule is free to rotate within that plane (Figs. 3D, 3H, 3L).

2.3 1-dimensional nonadiabatic alignment

Molecules can also be aligned with laser pulses that are much shorter than the rotational period [13]. A first experimental demonstration of such nonadiabatic alignment was reported recently by Vrakking *et al.* for the I_2 molecule [19]. They demonstrated one of the very attractive aspects of nonadiabatic alignment, namely that molecules can be aligned when the field is over. In particular, for linear molecules the field free alignment is repeated periodically in time (revivals) at instants separated by $1/4Bc$.

Recently, we have studied nonadiabatic alignment of iodobenzene with the purpose of achieving field free alignment [20]. Due to the more complex rotational structure of an asymmetric top molecule it is not obvious that the revival alignments will be very pronounced. Instead, we focused on the alignment obtained shortly after the alignment pulse [14–18]. Using a 3-ps-long, 3×10^{12} W/cm^2 pulse ($\lambda = 800$ nm) we demonstrated that the symmetry axis of iodobenzene molecules reaches a maximum degree of alignment $\sim$ 3 ps after the peak of the 800 nm pulse — *i.e.* under field free conditions. The alignment was probed by photodissociation with a timed 200 fs pulse ($\lambda = 266$ nm) and state selective ionization of the I photofragments by a delayed nanosecond laser pulse.

3 Control of photoabsorption

In general, absorption of polarized light by molecules depends on the alignment of the molecule with respect to the polarization direction. Therefore, by controlling the angle between the polarization vectors of an exciting laser field and an aligning laser field one can preferentially populate through photoexcitation a state of a given symmetry, while suppressing the population of states of different symmetries.

One example is single photon dissociation of I_2 molecules in the range 470–495 nm that occurs through excitation to either the B $^3\Pi_0$ or to the $^1\Pi_1$ state. Since the X→B transition is parallel and the X→ $^1\Pi_1$ is perpendicular strong selectivity of the two dissociation pathways is achieved simply by polarizing the dissociation field either parallel or perpendicular to the alignment field [21]. Another example is ultraviolet dissociation of iodobenzene that can proceed through a $n \rightarrow \sigma^*$ or a $\pi \rightarrow \pi^*$ transition. Some control of the two dissociation mechanisms is possible using 1-dimensionally aligned molecules [22]. However, since these two excitation channels are not pure parallel and perpendicular transitions, like in the I_2 example, a more complete control requires 3-D alignment. In general, for obtaining selective photoexcitation of asymmetric top molecules it is necessary to align them 3 dimensionally.

Absorption of light by molecules in the strong field limit leading, for instance, to multiple ionization is also strongly dependent on the angle between the molecular geometry and the polarization of the strong field [23–26]. As an example iodobenzene, 1-D aligned by a 3.5 ns YAG pulse, was irradiated by a 100 fs, 10^{14} W/cm^2 ($\lambda = 800$ nm) pulse polarized either parallel or perpendicular to the alignment field. The iodobenzene molecules were seeded in 1 bar of argon and $I_{\mathrm{YAG}} = 10^{12}$ W/cm^2. In Figure 4A the radial distribution [27] of the I^{2+} ions for the two polarization geometries is shown. The difference is striking — the yield of I^{2+} is more than a factor 17 larger when the ionizing field is polarized parallel rather than perpendicular to the symmetry axis. Although no calculations have been performed on iodobenzene it is likely that enhanced ionization is the primary reason for the difference. A similar experiment was performed on ICl [28] and the results is shown in Figure 4B. Again, the production of I^{2+} is much enhanced (by a factor of $\sim$ 6) when the ionizing field is parallel instead of perpendicular to the alignment field. In particular, it is seen that the 100 fs pulse is capable of removing up to six electrons from the ICl molecule when it is polarized parallel to the alignment field but not more than two electrons when it is polarized perpendicular to the field. For instance, the yield of the I^{2+}–Cl^{3+} channel, corresponding to five times ionization of ICl is $\sim$ 21 times larger in the parallel geometry compared to the perpendicular geometry. These observations agree well with the predictions of enhanced ionization theory [23,24].

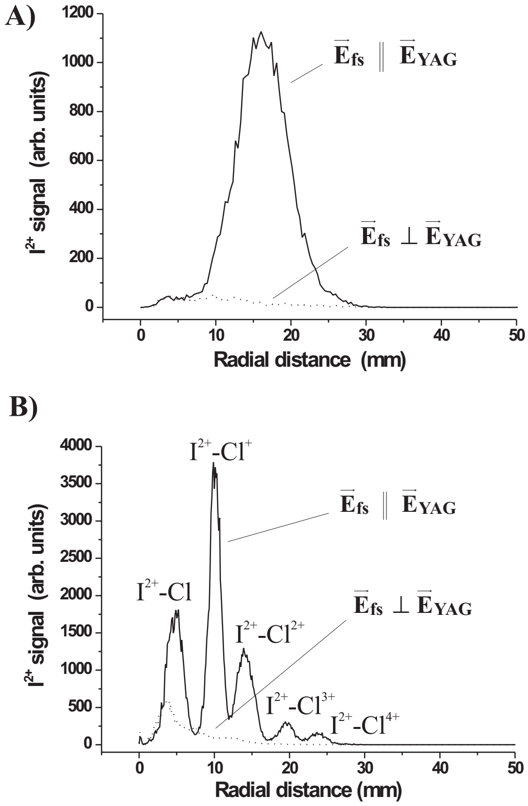

Fig. 4. The radial distribution (approximately proportional to the velocity distribution) of I^{2+} ions produced by irradiation of 1-D aligned (A) iodobenzene molecules or (B) ICl molecules with a 100 fs, $I = 10^{14}$ W/cm^2 pulse polarized along the alignment direction (full curve) or perpendicular to the alignment direction (dotted curve). The different ionization channels of ICl are marked above each of the peaks.

4 Conclusion / Outlook

Molecules can be adiabatically aligned 1-D, 2-D, or 3-D using a linearly, circularly, or elliptically polarized ns pulse, respectively, with an intensity in the range 10^{10}–10^{13} W/cm^2. Recent experiments show that nonadiabatic 1-D alignment with a few ps long linearly polarized pulses is also possible. Applications of adiabatically aligned molecules must occur in the presence of the strong field. In some cases it is possible to take advantage of the strong field — for instance in Raman type experiments [8,11]. In other cases where electronically excited states are involved the strong field can distort the experiment through further excitation or ionization of the state [9,20]. Nonadiabatic alignment offers an attractive alternative in terms of field alignment, although the time window in which the molecules are efficiently aligned is only a few picoseconds. Also, optimal pulse shaping might provide a stronger degree of alignment than what can be achieved in the adiabatic limit [29,30]. It is yet to be seen whether significant field free 3-D alignment can be obtained.

Aligned molecules will be useful in a number of areas including scattering of ultrashort electron pulses [31], high harmonic generation [32], time resolved photoelectron spectroscopy [33], and shaping and generation of ultrashort light pulses [34,35].

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