Direct Determination of the Sign of the NO Dipole Moment

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We report a novel approach for determining the sign of permanent dipole moments, using nitric oxide [NO($v = 0$)] as an example. State-selected NO ($j = |m| = |\Omega = 1/2$) molecules are focused using a hexapole and oriented in a strong dc electric field. The angular distributions of ionic fragments resulting from extreme ultraviolet single-photon and multiphoton dissociative ionization at 400 and 800 nm are measured and indicate that the dipole moment is negative (corresponding to $N^- O^+$). The experiments thus rule out an error in the sign of the dipole of NO as the possible source of a remarkable discrepancy between previous theoretical and experimental work on orientation effects in bimolecular collisions involving oriented NO.

As a result of extensive fundamental research, molecular ionization and dissociation in intense laser fields are now quite well understood [1]. Studies of atomic and molecular dynamics in intense laser fields have led to important spinoffs such as coherent light sources in the extreme ultraviolet (XUV) by high-order harmonic generation (HHG) [2] and new methods for measuring molecular structures [3] and wave functions [4,5]. Here, we present a study where HHG and recently acquired understanding on the alignment and orientation of molecules in strong laser and dc fields are used to determine the sign of the permanent dipole moment of NO in its ground state. This dipole moment has been the subject of a recent controversy [6], due to an unresolved sign discrepancy between measurements and calculations of the steric asymmetry for He-NO, Ar-NO, and D_2-NO rotationally inelastic collisions [6,7]. The steric asymmetry describes the orientation dependence of the (final state-dependent) collision cross section σ and is defined as

$$S = \frac{\sigma^{\text{Head}} - \sigma^{\text{Tail}}}{\sigma^{\text{Head}} + \sigma^{\text{Tail}}}. \quad (1)$$

For NO, a collision onto the N-end is considered to be a "head" collision. If $S > 0$, head collisions contribute more to a specific final rotational state $NO(j')$ than tail collisions. Experiment and theory agree that for Ar-NO, He-NO, and D_2-NO collisions S oscillates and changes sign as a function of final rotational state. However, while the absolute values of the experimental and theoretical steric asymmetry agree very well, their sign is *opposite*. The discrepancy would be resolved if the dipole moment of NO would be opposite to its *ab initio* value—i.e., N^+O^- instead of N^-O^+, inverting the NO orientation in the experiment [6].

The absolute value of the electric dipole of NO($v = 0, X^2\Pi$) was measured with high precision by Hoy *et al.*: $\mu_{NO} = 0.15740.014$ D [8]. This value slightly deviates from the *ab initio* value of 0.1732 D calculated by Langhoff *et al.* [9]. The latter authors predicted a negative

dipole moment, i.e., N^-O^+, which is supported by additional *ab initio* calculations [10]. The sign of a molecular dipole moment can in principle be obtained experimentally from the isotopic dependence of magnetic susceptibility factors [11]. However, for N_2O, this technique led to a sign opposing a theoretical calculation [12]. So far, even the highest precision measurements have been unable to determine the sign of the NO dipole moment experimentally [13].

In this Letter, we present a new approach towards measuring the sign of molecular dipole moments and apply it to NO. Measurements were carried out in four steps: namely (1) full state-selection of NO in the low-field seeking component of the rotational ground state using a hexapole focusing field, (2) orientation in a strong dc field, (3) dissociative ionization of the oriented NO using an XUV, a UV (400 nm), or a near-infrared (800 nm) light source, and (4) measurements of the angular distribution of ionic fragments using the velocity map imaging technique [14].

The interaction energy W for NO in relatively high dc fields is approximated by the first order Stark effect:

$$W^{(1)} = -\langle \mu \cdot E \rangle = -\mu E \frac{m\Omega}{j(j+1)} = -\mu E \langle \cos\vartheta \rangle. \quad (2)$$

Here, m and Ω are the projections of total angular momentum j onto the space-fixed z-axis (defined along electric field E) and on the internuclear axis, respectively, μ is the permanent dipole moment, and θ is the angle between the permanent dipole and the laser polarization axis. In Eq. (2), the internuclear axis points along the permanent dipole moment, i.e., from the negative towards the positive end of the molecule. In a hexapole [consisting of six hexagonally-assembled rods to which alternating negative and positive dc voltages are applied (see Fig. 1)] [15], molecules with $m\Omega > 0$ are in high-field seeking states and are pulled towards the hexapole rods, while molecules with $m\Omega < 0$ are in low-field seeking states and are pushed towards the center of the hexapole.

Without any dc electric field present, each rotational state of NO consists of a Λ-doublet, i.e., a symmetric or antisymmetric linear combination of symmetric top wave functions. In a dc field, the two components of the Λ-doublet are mixed and turn into a high-field seeking and a low-field seeking state. In Hund's case (a), the orientation probability distribution of these states in a relatively high dc electric field is given by

$$W(\theta) = |\Psi_{j,m,\Omega}|^2 = |d^j_{m,\Omega}(\theta)|^2. \quad (3)$$

For low- and high-field seeking states with $j = 1/2$, it follows that

$$W(\cos\theta) = \frac{1 - \cos(\theta)}{2} \quad \text{for} \quad j = 1/2, \quad m = \pm 1/2, \quad \Omega = \mp 1/2, \quad \text{low-field seeking}$$

$$W(\cos\theta) = \frac{1 + \cos(\theta)}{2} \quad \text{for} \quad j = 1/2, \quad m = \pm 1/2, \quad \Omega = \pm 1/2, \quad \text{high-field seeking}. \quad (4)$$

Molecules in the low-field seeking state that are placed in a dc orientation field orient with their negative end towards the negative electrode. To determine which side of the molecule this corresponds to, dissociative ionization in combination with angular-resolved mass-spectrometric detection can be used (see Fig. 1), provided that the orientation is not altered by the laser and that the dissociation process occurs on a time scale that is much shorter than the rotational period of the molecule (10 ps). In the experiment (see Fig. 1), a mixture of 10% of NO in Ar (1.6 bar) expanded from a General Valve operated at 15–25 Hz. Following a Ø = 1 mm collimator placed at 5 cm from the nozzle, the beam entered a hexapole state selector, placed 25 cm further downstream. The inscribed radius and the diameter of the 1 m long hexapole rods [16] were both 4 mm. Using a 10 kV voltage difference between the hexapole rods, selected NO molecules were focused into a velocity map imaging spectrometer (VMIS) [14], placed 30 cm downstream. The VMIS consisted of an extraction region, a drift region, and a dual microchannel plate detector (MCP) followed by a phosphor screen and a camera system to record the positions of ion impact. In the VMIS, the NO molecules were oriented by the applied 13 kV/cm

extraction field and dissociatively ionized. The polarization axis of the laser was tilted with respect to the detector axis. Consequently, an asymmetry in the recoil velocity distribution of the fragment ions caused by orientation of the parent molecule (with respect to the detector axis) leads to an asymmetry in the fragment velocity distribution in the plane of the velocity map imaging detector (see Fig. 1) [17]. We note that our temporal resolution did not allow determination of the molecular orientation from flight time differences (~1 ns) for fragments initially moving towards or away from the detector. To distinguish N^{q+} and O^{q+} (with q being the charge state), a fast Kentech SPSV (12 ns, −1 kV into 50 Ω) pulse-generator was used to gate the frontside of the MCP detector. A positive dc voltage was applied to the backside of the MCP detector. Hence, for a duration of (at most) 12 ns, the detector operated at full gain, whereas outside this time window, the detector operated at a gain that was reduced by appr. 3 orders of magnitude, allowing selective detection of N^{q+} or O^{q+}.

In Fig. 2, 2D velocity maps are shown for detection of N^+ resulting from XUV dissociative ionization. To generate the XUV, a 2 mJ 50 fs Ti:Sapphire laser was focused onto a pulsed Ar jet using a 1 m lens. The divergent XUV beam, containing a superposition of harmonics, intersected the NO beam at right angles. The intensity of the Ti:Sapphire laser at the interaction region was $3–4 \times 10^{10}$ W/cm^2, i.e., too low to influence the dissociation. Velocity maps were recorded with the XUV polarization at $\alpha = \pm 45°$ with respect to the dc electric field axis and show that the N^+ ions favor an "upward" recoil, consistent with the N-end of the molecule being negative and the O-end being positive (N^-O^+). The absence of detectable O^+ fragments suggests that $N^+ + O$ and $N^+ + O^-$ were predominantly formed. O^- ions were observed, but not in sufficient quantities to allow measurement of a velocity map.

Experiments were also performed using intense 400 and 800 nm light from the same fs Ti:Sapphire laser. Figure 3 shows N^{2+} and O^{2+} velocity maps obtained by Coulomb explosion of NO at 800 nm, using ≤ 4 mJ 50 fs Ti:Sapphire laser pulses focused with a 20 cm lens. The 800 nm experiments show the effect of geometric and/or dynamic alignment [1]. Strong field ionization processes
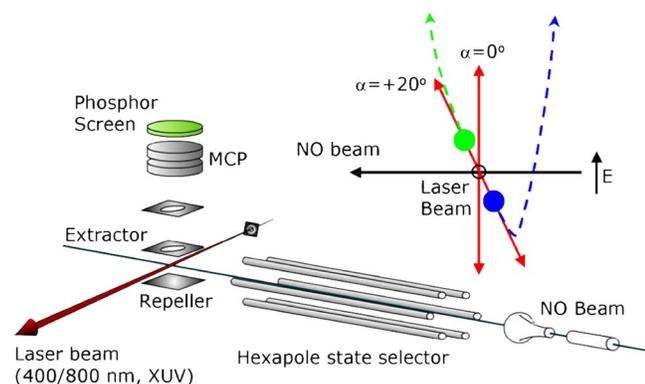

FIG. 1 (color online). Schematic representation of the experiment. NO molecules are state-selected using a hexapole and oriented in the 13 kV/cm extraction field of a velocity map imaging spectrometer. They are dissociatively ionized using fs XUV radiation or 400/800 nm radiation from an intense fs Ti:Sapphire laser. The laser polarization is tilted with respect to the detector axis, so that ions moving upwards or downwards after the dissociation can be distinguished.
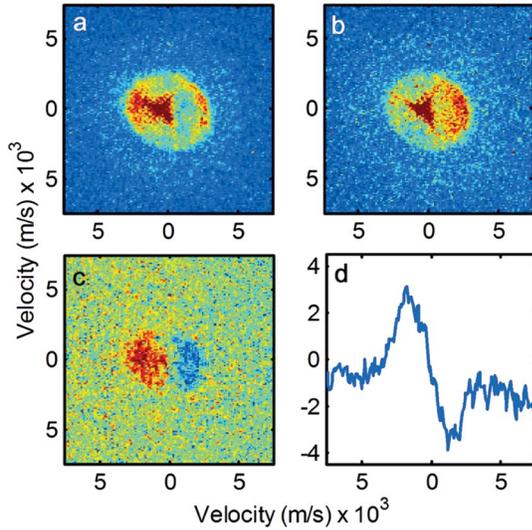
FIG. 2 (color). 2D Velocity maps for N^+ fragments from dissociative ionization of oriented NO by a fs XUV pulse, with $\alpha = +45°$ (a) and $\alpha = -45°$ (b). The difference between (a) and (b) is shown in (c). Figure (d) results from integration along the y axis of (c). For $\alpha > 0$, the N^+ fragments are more abundant in the left part of (a), indicating that in the oriented NO sample, the N-atoms face the negative electrode. This is consistent with the negative charge of the dipole being on the N-atom. The central dot in the images is due to partial detection of NO^+ caused by the DC component of the time dependent voltage applied to the MCP.
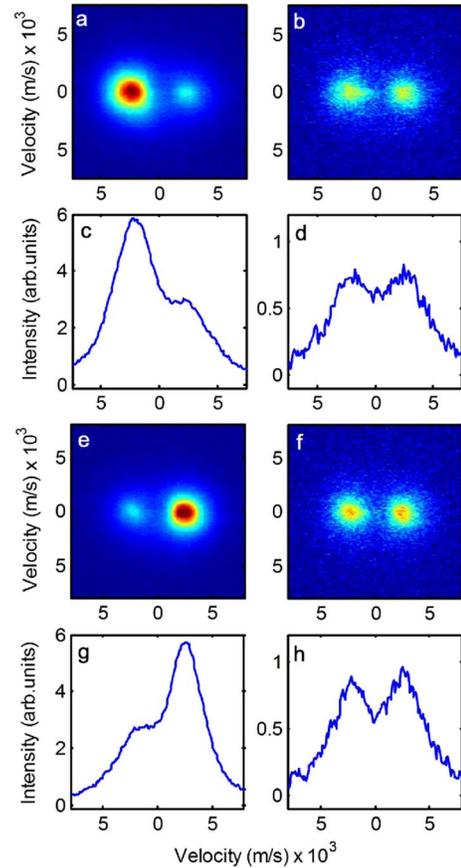

FIG. 3 (color online). 2D Velocity maps for detection of N^{2+} and O^{2+} fragments resulting from dissociative ionization of NO by an intense 50 fs 800 nm pulse with $\alpha = +20°$. Figures (a) and (b) show N^{2+} results with the hexapole on (a) and off (b), while (e) and (f) show this information for O^{2+}. Figures (c), (d), (g), and (h) result from integration along the y axis of the velocity maps shown above. With the hexapole off, the N^{2+} and O^{2+} fragments are symmetrically distributed. With the hexapole on, N^{2+} appears predominantly on the left and O^{2+} predominantly on the right. This indicates (see Fig. 1) that in the oriented NO sample, the N-atom faces the negative electrode and is consistent with the negative charge of the dipole being on the N-atom.

tend to favor molecules that are aligned along the polarization axis of the ionizing laser ("geometric alignment"). In addition, molecules experience a torque and are dynamically aligned [18,19]. While dynamic alignment facilitates the visibility of the orientational asymmetry, it is a possible source of error if the laser system contains prepulses. Given that the production of N^{2+} and O^{2+} ions by Coulomb explosion requires intensities of $O(10^{15} \text{ W/cm}^2)$, prepulses with an intensity of ~0.1% of the main peak are sufficient to alter the molecular orientation before it is probed [20]. Indeed, we have observed that at 800 nm, the observed asymmetry disappears when the peak intensity at the focus of the laser becomes too high [21].

In Fig. 3, a comparison is presented of N^{2+} and O^{2+} velocity maps at 800 nm with the voltage on the hexapole rods turned on or off. In the former case, the NO molecules are state-selected and the experiment uses an oriented sample, while in the latter case, equal numbers of high-field seeking and low-field seeking NO molecules are present in the laser focus which orient in opposite directions. Consequently, no net orientation is expected and no asymmetry is observed. Conversely, when the hexapole state-selector selects low-field seeking states, the signal increases by an order of magnitude, and a pronounced asymmetry is observed, which confirms the orientation of the NO molecules with the N-side towards the negative electrode.

To alleviate the problem of dynamic alignment by prepulses, further experiments were performed using the 2nd

harmonic of the fs Ti:Sapphire laser at 400 nm, generated by using a 1 cm KDP crystal ($\tau_{UV} \approx 750 \text{ fs} \ll T_{rot}$). Figure 4 shows N^{2+} and O^{2+} velocity maps from experiments where the 400 nm polarization was at $\alpha = +30$ and -30 degrees with respect to the dc electric field axis. The influence of dynamic and/or geometric alignment is again visible. However, since 2nd harmonic generation is a nonlinear process, the influence of prepulses no longer needs to be considered. The results in Fig. 4 show once more that the low-field seeking states selected by the hexapole orient with the N-side towards the negative electrode, confirming our conclusion that in the dipolar NO molecule the negative charge is on the N-end and the positive charge is on the O-end. Hence, all three experiments rule out that an error in the sign of the dipole moment of NO is responsible for the long-standing discrepancy between experimental and
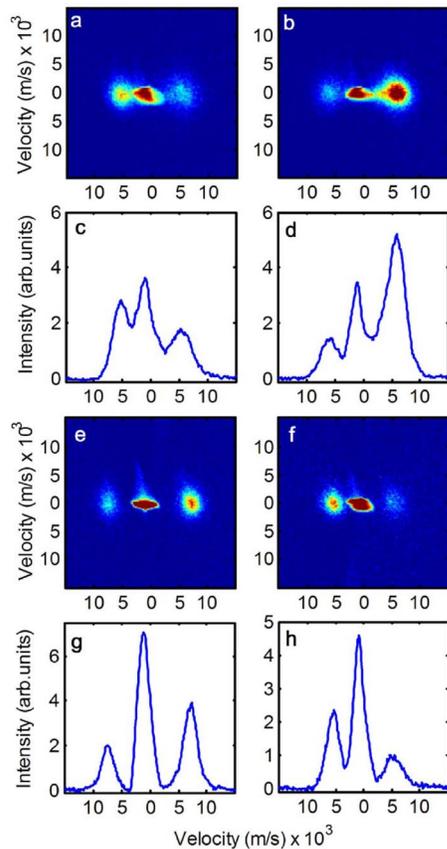
FIG. 4 (color online). 2D Velocity maps for N^{2+} and O^{2+} fragments resulting from dissociative ionization of oriented NO by an intense 750 fs 400 nm pulse. Figures (a) and (b) show N^{2+} results for $\alpha = +30°$ (a) and $\alpha = -30°$ (b), while (e) and (f) show this information for O^{2+}. Figures (c), (d), (g), and (h) result from integration along the y axis of the results shown above. For $\alpha > 0$, the N^{2+} fragments appear predominantly on the left and the O^{2+} fragments predominantly on the right, while for $\alpha < 0$, the situation is reversed. This indicates (see Fig. 1) that in oriented NO molecules, the N-atom faces the negative electrode and is consistent with the negative charge of the dipole being on the N-atom. Similar to Fig. 2, the central dot in the images is due to partial detection of NO^+ caused by the DC component of the time dependent voltage applied to the MCP.

theoretical results on the orientation dependence of Ar-NO, He-NO and D_2-NO collision experiments. In addition, our experiments open a new chapter in experimental work on strong field manipulation of the external degrees of freedom of molecules. In the last decade, significant progress has been made on strong field molecular alignment, where the state-of-the-art is now 3D alignment of cold molecules under field-free conditions [22]. Sakai and co-workers have so far obtained the only results on molecular orientation [23]. However, their method is only suited for relatively heavy molecules that orient in low electric fields and a very modest degree of orientation was observed. In our experiment, the use of a hexapole introduces the possibility to perform strong field alignment and orientation experiments with a state-selected molecular beam, thereby im-

proving the degree of alignment and orientation that can be achieved and providing experimental access to the full quantal information of an alignment or orientation process.

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