$I > 2\sigma(I)$), $R_1 = 0.0768$, $wR_2 = 0.1153$ (for all data); data-to-parameter ratio 16.52; residual electron density $+0.302/-0.260$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158650. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

IR-UV Double-Resonance Photodissociation of Nitric Acid ($HONO_2$) Viewed as Molecular Information Processing**

Thomas Witte, Christine Bucher, Françoise Remacle, Detlev Proch, Karl L. Kompa, and R. D. Levine*

One route to nanoscale computing is to make single molecules that can mimic the function of conventional components of electronic logic circuits, such as switches or wires. There is therefore increasing activity in producing molecules that can conduct electrical current or can be instructed to turn it on or off when placed within a suitable support. This field of activity, sometimes known as molecular electronics[1] or molecular scale electronics,[2] is a major current research area. Now that several groups[2–4] have demonstrated that a molecule can act as a switch,[5] it is possible to begin thinking about replacing transistors by single molecules within larger digital devices. The chemical pumping of molecules in solution that induces changes that can be optically detected has also been been studied for some time[6–8] as a possible route to logic gates. More generally, the progress in supramolecular chemistry towards the construction of molecular machines[9, 10] opens up many possibilities for an induced response.

An alternative to the approach in which a molecule acts as a single switch is a scheme where the function of an entire logic circuit is performed by a single isolated molecule.[11, 12] A particular molecular coordinate, which could be a reactive one, acts as the bus for information transfer. This alternative route has the distant goal of incorporating the logic capabilities of a complete integrated circuit on a single molecule. A more modest goal is the experimental demonstration of a circuit containing several connected logic gates as a (logic) equivalent of the intramolecular dynamics of a single molecule. The experimental demonstration of such a scheme is presented herein.

A molecule in a molecular logic gate scheme[11] becomes a vehicle for information processing, where the input is optical excitation. In the experiment discussed below the resonance requirement is paramount, and an intramolecular motion is essential for the logic action. We discuss time-resolved measurements because one advantage of our gates is that they can be ultrafast, as reported for a number of other systems.[11] With our device we get the output as an optical signal. However, the recent experiments of Crim and coworkers[13] suggest that the logic of the present approach can be probed by chemical means.

A conventional logic circuit is built from connected switches. The advantage of the approach we follow is that by operating a single molecule as a logic circuit one avoids the need to connect switches. The circuit reported here is already equivalent to several switches, and this, we hope, is only the beginning. The logic gate that we describe is completely irreversible since the molecule is destroyed. This dissociation is not an essential aspect and we have discussed[11] other molecules where this need not be the case, and where the initial state can be recovered as quickly as one picosecond.

The power of organic synthesis to design molecules should not be overlooked. What one wants is a circuit that is operable over many cycles. The first step is the need to regenerate the ground state. In some systems, for example, the photoinduced keto–enol tautomerism, this requirement is inherently satisfied. In other systems, such as electrocyclic ring openings, the photoprocess generates more than one possible product, and this can be used to advantage. In essence what we look for is a prompt intramolecular response to an optical excitation. Typically, such a response involves a rotation of part of a molecule relative to another to bring about a recoupling of the electronic orbitals.

Since the 1970s great advances have been made possible by combining laser spectroscopy and reaction dynamics. The double-resonance experiment that we discuss falls into this class. The principles[14–16] are understood and the application to the $HONO_2$ system has been previously studied.[17, 18] What is new and interesting is the hitherto unknown effect determined by the order of the two ultrafast UV and IR pulses. Still, it can be asked if what we are discussing is little more than a semantic rephrasing of an experiment. What we actually do is to explore the implications of a spectroscopic experiment from a new point of view, which opens up options and possibilities that are not evident without it. It also raises new questions of principle. For the moment, however, we just want to highlight a cross-disciplinary study involving modern chemical physics and Boolean logic. We are aware that one can carry our ideas into the non-Boolean (that is, quantal) regime, but for now we will view the experiment in chemical kinetic, that is, classical, terms.

To introduce the subject we begin with the IR-UV double-resonance experiment of Crim and co-workers (Figure 1).[14, 17–19] An IR photon generates a vibrationally excited state (OH stretch overtone) of the ground electronic state of

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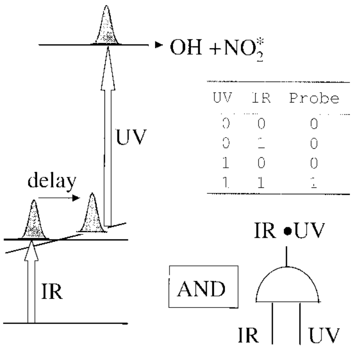

Figure 1. A schematic drawing of the IR-UV pumping scheme for a positive delay time and the corresponding AND gate. The truth table is also shown. The energy level scheme indicates that there should be a delay after the absorption of the IR pulse so that the energy can redistribute before absorption of the UV photon. Two intermediate levels are shown so as to indicate that there is an intramolecular process that takes place during the delay between the two pulses. The AND logic gate is shown as a semi-circle. The lines show the inputs and outputs using a Boolean notation so that, for example, ω_{UV} has the value 0 or 1 when a UV laser pulse is not used or is applied to the molecule, respectively. The output ($\omega_{IR}\omega_{UV}$) is detected as the fluorescence of NO_2^*. The value of the output, corrected for background as discussed in the Experimental Section, is zero unless both lasers are on.

$HONO_2$. A second, this time UV, photon takes the molecule up to the (second[20, 21]) electronically excited level from which the reactive process initiates. In principle (see Experimental Section) the UV photon does not have sufficient energy on its own to access this level. The reactive process, dissociation to $OH + NO_2^*$, results in an observable fluorescence from the electronically excited NO_2^* species. This experiment by itself is equivalent to the logic AND gate[22] (shown as a semi-circle in Figure 1), since an output signal is possible only if both input photons are "on". The truth table for this gate is also shown in Figure 1.

The dynamics for the above kind of experiment have been thoroughly discussed.[14, 17–19] The time delay after excitation with the IR photon is necessary for redistribution of the energy in the ground electronic state of HNO_3. The time scale is established by delaying the femtosecond-long UV signal. It takes about 12 ps (Figure 2) for the necessary intramolecular vibrational relaxation (IVR), as characterized by the time taken for the NO_2^* fluorescence to reach a maximum. The electronic fluorescence of NO_2^* decays on a nanoscale time scale.

An AND gate is not a universal logic gate. Several universal logic gates are known, with the most familiar being the "NotAND" gate, which is usually written as "NAND".[22] To make a "NAND" gate we also need to know when "neither photon beam is on". To build the equivalent of a NAND gate one has to monitor the depletion of ground-state HNO_3. Since this is not an easy experiment, we have followed a quite different route.

We allow the UV signal to either be delayed or ahead of the IR pulse. This process gives us a new Boolean variable, the delay time τ. When $\tau=1$, one has the usual setup: IR signal first and UV signal delayed. But when $\tau=0$, one has the counter-intuitive arrangement where the UV signal is applied before the IR signal. An input equivalent to $\tau=0$ is $\bar{\tau}=1$, where the bar denotes the negation of the Boolean variable. The choice of $\tau=1$ or 0 is operational and is determined by the arrangement of the delay line (see insert in Figure 2).

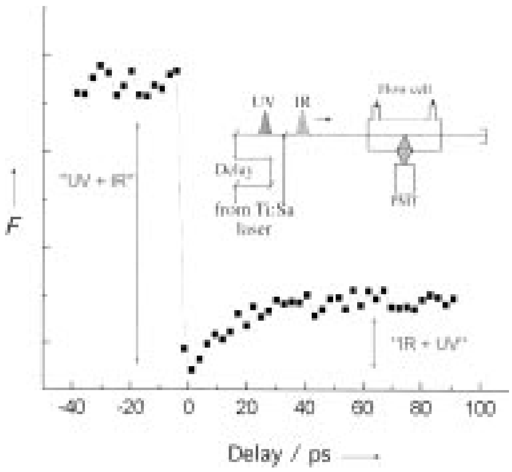

Figure 2. The (single photon) count rate for the fluorescence (F) of NO_2^* versus the delay time between the femtosecond-long IR and UV laser pulses. A positive delay time was used in the arrangement of Crim and co-workers, where the IR pulse is the first to be on, as shown in the insert (PMT = photomultiplier). A negative delay time is the counter-intuitive arrangement, where the UV pulse is first on. Note the sub-picosecond time taken for the fluorescence of NO_2^* to increase to a maximum when the delay time is negative. The count rate is corrected for the background as discussed in the Experimental Section.

The experimental results for the fluorescence of the NO_2^* species versus the physical delay time between the femtosecond-long IR and UV signals are shown in Figure 2. The right-hand side ($\tau > 0$) of the plot reproduces the experiment of Crim and co-workers.[17] The left-hand side ($\tau < 0$), however, is new and quite different. It shows that the same (to within experimental error) fluorescence signal for NO_2^* is observed for either sign of the delay time. However, for a negative delay, the time taken for the increase in the NO_2^* fluorescence signal is sub-picosecond. For a delay of one to several picoseconds, one can categorically distinguish between the variables τ and $\bar{\tau}$. We emphasize again that the distinction is not based on any difference in the character of the fluorescence spectrum, but on the sign of the delay time (provided that it is of the order of a picosecond). The experimental observation that negative and positive values of the delay time are distinguishable makes the experiment logically equivalent to the logic circuit shown in Figure 3.

The circuit shown has four gates. The lines connecting them are for visualization purpose only and indicate which variables are input to which gate. The circuit is equivalent to the dynamics of only one molecule, and by using single photon counting (as shown in Figure 2) fewer than 10^3 events are sufficient to result in a reasonable signal to noise ratio, particularly so if the distinction between τ and $\bar{\tau}$ is made around one picosecond. The elements of the circuit are: a) an AND gate, as in Figure 1, which yields the output 1 only if both photons are present; b) a NOT gate, shown as a triangle,[22] which is a simple one-input gate such that the output is 1 or 0 if the input is 0 or 1; c) an AND gate, to the

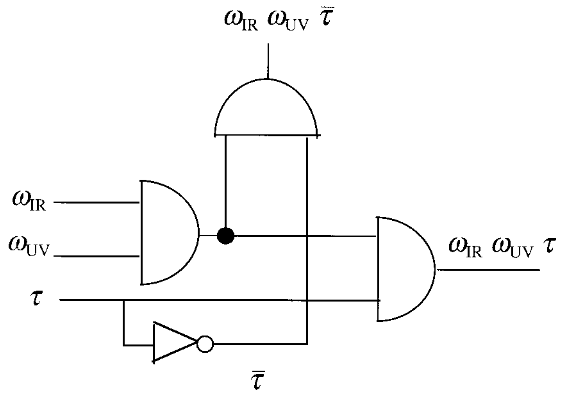

Figure 3. The logic circuit which is the equivalent of the experiment described in Figure 2 when the NO_2^* fluorescence is detected after a short time (around a picosecond). τ is the Boolean variable whose value is 1 if the delay time is experimentally set to be positive and 0 if it is negative. $\bar{\tau}$ is the logic complement of τ. The complementary variable is generated by a NOT gate (shown as a triangle). The two distinct outputs, $\omega_{IR}\omega_{UV}\tau$ and $\omega_{IR}\omega_{UV}\bar{\tau}$, are detected by experimentally gating the fluorescence count of NO_2^* to short (of the order of picoseconds) times. The gates are connected because the output of the first AND gate, the one shown in Figure 1, can be detected for either value of τ.

right of the figure, whose output is 1 only when both photons are present and the time delay is positive; and d) an AND gate whose output is 1 only when both photons are present and the time delay is negative. The circuit shown in Figure 3 is not meant to have a 1:1 correspondence with the experimental setup, it is meant to perform the same logic (compute a Boolean function) as implemented by the experiment. There are 2^{2^n} Boolean functions of n Boolean variables and the function $\omega_{IR}\omega_{UV}\bar{\tau}$ is not the logic complement of the other function $\omega_{IR}\omega_{UV}\tau$.

At the moment it cannot be established with certainty why the counter-intuitive pulse sequence works. The photochemical interpretation is that by applying the UV pulse first, one accesses a lower, quasibound electronically excited state that is dissociated by the subsequent IR pulse. The known theoretical results[20, 21] for the electronic states of HNO_3 are not inconsistent with this possibility, but one cannot rule out a photophysical route, similar to that known for STIRAP pumping,[23] where the first UV photon couples the ground state and the second electronically excited state. Experiments using better count rates are in progress for the purpose of elucidating this point.

An alternative to the route that we discuss here, and a route that allows a chemical reading of the output, is provided by the recent experiment of Crim and co-workers[13] on controlling the Cl + HNCO reaction. This experiment has a double-resonance part as discussed earlier, but the vibrationally excited ground-state HNCO molecule is given another dynamic option, namely to react with a Cl atom. In this way, the Cl atom that does not react with a vibrationally cold HNCO molecule probes the IR absorption.

We have shown how the different intramolecular dynamics of HNO_3 when excited to different states (vibrational overtone of the ground electronic state versus an excited electronic state) can be used to represent connected logic circuits. This confirms our suggestion[11] that molecular motions can be used as a bus for the purpose of information processing. We have also shown how the direction of time can be used as a logic variable.

Experimental Section

The experimental arrangement (Figure 2) was adapted from the design of Crim and co-workers.[17] The key difference is the option of a negative delay time between the femtosecond-long IR and UV pulses. The sign of the delay time is determined by the mechanical arrangement of the mirrors and is set before the lasers are switched on. This arrangement is the logic equivalent of the NOT gate. For a positive time delay, the experiment reproduces the reported results.[17] There is some signal from the UV pulse alone on both sides of the zero delay, presumably as a result of the dissociation of hot molecules. This background signal was subtracted from the count rate reported in Figure 2.

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