Quantum Computation with Vibrationally Excited Molecules

Carmen M. Tesch* and Regina de Vivie-Riedle†

MPI für Quantenoptik, 85741 Garching, Germany

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A new physical implementation for quantum computation is proposed. The vibrational modes of molecules are used to encode qubit systems. Global quantum logic gates are realized using shaped femtosecond laser pulses which are calculated applying optimal control theory. The scaling of the system is favorable; sources for decoherence can be eliminated. A complete set of one- and two-quantum gates is presented for a specific molecule. Detailed analysis regarding experimental realization shows that the structural resolution of today's pulse shapers is easily sufficient for pulse formation.

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The possibilites offered through quantum computation have been well known for almost 20 years [1,2]. In the last few years the first basic ideas for realization have been discussed and experimental efforts have been made using cavity quantum electrodynamics [3], trapped ions [4], and nuclear magnetic resonance [5,6].

In this Letter we demonstrate how to use vibrational modes of molecules in an ensemble for complete quantum computation processes. In an N-atomic molecule 3N-5 (or 3N-6) normal modes can be identified, and each of these normal modes can be used to define a quantum bit. Two different excitations in each mode are referred to as $|0\rangle$ and $|1\rangle$. To implement quantum logic operations in this qubit system, shaped femtosecond laser pulses in the IR-regime are used. They are designed with the help of optimal control theory (OCT) [7,8] which are in principle realizable in pulse shaping experiments [9,10]. The system inherent interaction between different qubits is mediated via the molecular bondings.

For initial state preparation again shaped femtosecond laser pulses are used. They can be calculated with our standard OCT algorithm which can also compensate for rotations of molecules in the gas phase [11,12]. Vibrational state preparation is optionally possible for the vibrationless ground state, fundamentals, overtones, and combination modes as in the present work. Maximally two shaped femtosecond laser pulses of different wavelengths are needed for preparation.

The detection of states after a computation can be achieved by applying standard laser diagnostics (for example, time resolved IR spectroscopy [13], laser induced fluorescence spectroscopy [14], stimulated emission pumping, or resonant multiphoton ionization [15]).

In the following part of the Letter we will show that vibrationally excited molecules provide a realistic physical system to implement a quantum computer. We will demonstrate a realization of the above ideas using acetylene (C_2H_2) as a two-qubit model system. Our new OCT-functional, laser pulses for elementary global one- and two-quantum gates (which form a universal quantum gate altogether [16]), and the preparation of entanglement will be presented. An analysis of the shaped femtosecond laser pulses will show that these pulses are simply structured. The problem of decoherence is discussed and a solution is found. Error detection is also feasible.

OCT is a very powerful tool for calculating laser pulses guiding a quantum system to any selected objective; in particular, the preparation of eigenstates is enabled. In this case, the goal in OCT is to find a laser field $\varepsilon(t)$, which drives a system from initial states $\psi_{ik}(0) = \phi_{ik}$ at time $t = 0$ to final target states ϕ_{fk} at a fixed time $t = T$. The initial and target states correspond with the eigenstates defining our qubits. The calculated laser pulses $\varepsilon(t)$ represent the quantum gates.

Algorithmic schemes allow the formulation of the optimization problem in terms of the maximization of the functional

$$K(\psi_{ik}(t), \psi_{fk}(t), \varepsilon(t)) = \sum_k |\langle\psi_{ik}(T)|\phi_{fk}\rangle|^2 - \int_0^T \alpha|\varepsilon(t)|^2 dt - 2\Re\left[\langle\psi_{ik}(T)|\phi_{fk}\rangle \int_0^T \langle\psi_{fk}(t)|\left(\frac{i}{\hbar}[H_0 - \mu\varepsilon(t)] + \frac{\partial}{\partial t}\right)|\psi_{ik}(t)\rangle dt\right]. \quad (1)$$

The first term gives the overlap between the laser driven wave function $\psi_{ik}(t)$ and the desired target states ϕ_{fk}; the second one represents the laser field $\varepsilon(t)$ which drives the system wave functions towards the target states with a limited field intensity (penalty factor α). The last term ensures that the time dependent Schrödinger equation is fulfilled. H_0 and the dipole moment vector field μ have been calculated *ab initio*, which means that all molecular characteristics of the electronic and nuclear movement and their interactions are exactly implemented in the calculations.

Varying the above functional with respect to its variables and searching for $\delta K = 0$ leads to a set of $2k + 1$

coupled differential equations. The solution is found iteratively and results in the optimal quantum gate $\varepsilon(t)$ as a self-consistent solution to this system.

The new feature which is of highest importance in the context of quantum computation is the fact that we are able to optimize k transitions simultaneously with the above new functional. Its recent implementation in our algorithms enables us to calculate globally applicable quantum gates, because for each basis state of our qubit system the correct transition k is optimized, and undesired transitions can be explicitly suppressed. For example in a two-qubit system a global NOT pulse in the second qubit has to fulfill $|00\rangle \rightarrow |01\rangle$, $|01\rangle \rightarrow |00\rangle$, $|10\rangle \rightarrow |11\rangle$, and $|11\rangle \rightarrow |10\rangle$ at the same time.

These basic principles for concrete quantum computation with vibrational modes are now discussed for an example system: acetylene. C_2H_2 contains five normal modes ($n_1 n_2 n_3 n_4 n_5$) in the electronic ground state (n_4 and n_5 are doubly degenerate). The asymmetric CH-stretching (n_3) and the *cis*-bending mode (n_5) are IR active. We have chosen them to define our two-qubit system [17] because direct experimental access is possible. One quantum in each mode is referred to as $|0\rangle$ and two quanta as $|1\rangle$ (other definitions would also have been possible). Our complete two-qubit system is described with the following four basis states: $|00\rangle := (00101)$; $|10\rangle := (00201)$; $|01\rangle := (00102)$; $|11\rangle := (00202)$.

We have computed a two-dimensional *ab initio* potential energy surface (PES) using a standard quantum chemical package (GAUSSIAN98 [18]). One system-adapted coordinate is sufficient for the description of one IR-active mode, because the relative distance between the two hydrogen atoms and the relative distance between the two carbon atoms rests constant during the motion (coordinates: $R \rightarrow$ *cis*-bending mode, $d \rightarrow$ asymmetric CH-stretching mode; see [12]). We solved the nuclear Schrödinger equation for our PES on a grid and calculated 80 eigenfunctions up to an energy of 23 150 cm^{-1} (the minimum energy is set to zero) applying a relaxation method [12]; four of them define our qubit basis. For the laser-matter interaction we have computed the *ab initio* dipole moment vector field, which can be decomposed into two parts, each part being responsible for the excitation of one IR-active mode. This decomposition and the energetic spacing between the two vibrations ensure a very specific excitation of each mode [R: 727 cm^{-1} (13.75 μm), d: 3289 cm^{-1} (3.04 μm)]. For the construction of our quantum gate $\varepsilon(t)$ the set of coupled differential equations is solved quantum dynamically applying the split operator scheme for the wave packet propagations.

With our new functional we have constructed global laser pulses for the following elementary one-quantum gates: identity operation $\mathbb{1}$ (trivial case or explicitly computed, $\mathbb{1} : |0\rangle\langle 0| + |1\rangle\langle 1|$), bit flips (NOT : $|0\rangle\langle 1| + |1\rangle\langle 0|$), phase shifts of π ($\Pi : |0\rangle\langle 0| - |1\rangle\langle 1|$), and the Hadamard transformation in the second qubit ($\mathrm{H} : |0\rangle \rightarrow \frac{1}{\sqrt{2}}[|0\rangle + |1\rangle]$ and $|1\rangle \rightarrow \frac{1}{\sqrt{2}}[|0\rangle - |1\rangle]$). The case for the first qubit is analogous. As a conditional two-quantum gate we have calculated a controlled NOT (CNOT) with the first qubit acting as the control state: $|00\rangle \rightarrow |00\rangle$; $|01\rangle \rightarrow |01\rangle$; $|10\rangle \rightarrow |11\rangle$; $|11\rangle \rightarrow |10\rangle$.

Exemplarily the optimized laser field for the CNOT gate is presented in Fig. 1. The first part of the figure displays the quantum gate $\varepsilon(t)$ versus time; the second one depicts a fast Fourier transform to analyze the spectral width and components of the laser pulse. It is not Fourier limited, and pulse shaping is needed to form this electric field with a broad spectral range. The last part of Fig. 1 analyzes the pulse structure in the time and frequency domain simultaneously mirroring the temporal ordering of the frequency components. The substructure is significant and rather symmetric in time.

For the realization of all our quantum gates our method needs only one single shaped laser pulse; a preceding special state preparation or pulse sequence is not necessary as in other approaches. We have analyzed the mechanism according to which our quantum gates work. In all cases not only states belonging to our qubit system, but temporarily energetically higher and lower lying vibrational levels are populated following a ladder climbing scheme. An intermediate coherent state is built up before all population is transferred into the desired eigenstates. These eigenstates are stable, no refocusing pulses are needed as in NMR quantum computing.

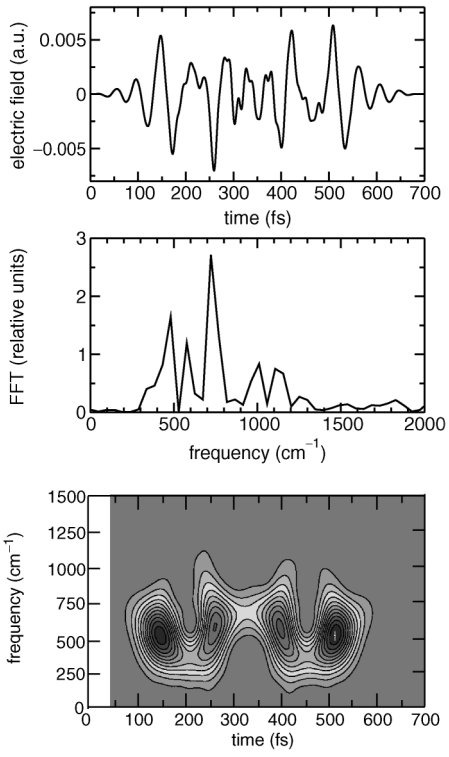

FIG. 1. Controlled NOT gate for a two-qubit system in vibrationally excited acetylene. Depicted are the strength of the electric field, a fast Fourier transformation, and frequency versus time. The efficiency of the gate is $\geq 90\%$.

The ratios r [defined as $|\langle\psi_{ik}(T)|\phi_{fk}\rangle|^2$] we can reach are $r(\mathrm{NOT}) \geq 91\%$; $r(\pi) \geq 97\%$; $r(\mathrm{Hadamard}) \geq 90\%$; and $r(\mathrm{CNOT}) \geq 90\%$. (For comparison, in cases of state preparation with $k = 1$ we can always reach efficiencies of $\geq$ 98%.) In each case the laser pulse found by the OCT algorithm consists of several structural units, and the total laser-matter interaction time is about 700 fs. The range of the frequency width is between $200\,\mathrm{cm}^{-1}$ (π pulse) and $560\,\mathrm{cm}^{-1}$ (CNOT pulse). The strength of the electric field e is moderate except for the NOT operation, but still below the ionization limit [maximum strength: $e(\mathrm{NOT}) = 0.0224$ a.u. $(7.146 \times 10^{13}\ \mathrm{W/cm^2})$; $e(\pi) = 0.0057$ a.u. $(1.1597 \times 10^{12}\ \mathrm{W/cm^2})$; $e(\mathrm{Hadamard}) = 0.0095$ a.u. $(3.226 \times 10^{12}\ \mathrm{W/cm^2})$; $e(\mathrm{CNOT}) = 0.0070$ a.u. $(1.749 \times 10^{12}\ \mathrm{W/cm^2})$]. First investigations in other systems show that the field strengths can be lowered down [19].

We also prepared entangled states. The efficiency or fidelity of our Bell state preparation (starting at one of our basis states and proceeding via a Hadamard state) is $r \geq$ 96% in each case. One part of the preparation of $\frac{1}{\sqrt{2}}[|00\rangle + |11\rangle]$ is shown in Fig. 2.

The prepared Bell state is not a long-lived normal mode, but a superposition state. In that context it is relevant to investigate the time evolution of the corresponding wave function. In Fig. 2 we have depicted the time evolution of the real part of our wave packet after the preparation of a Bell state. The wave function (real and imaginary parts) develops in time systematically, and $|\psi|^2$ comes back in predictable intervals. Its evolution in space is confined to a certain area. Once again one does not need refocusing pulses.

To realize our calculated gates, pulse shaping techniques are needed. In the spectral range from 430 nm to 1.6 μm liquid crystal modulators are already commercially available, having typically 128 discrete pixels. Powerful lasers operating in the midinfrared already exist [20]). Pulse shapers that work in the mid-IR and far-IR spectral ranges are actually under development, and new types of nonlinear crystals are explored [21]. Anyhow, a realization of a pulse shaper in the mid-IR and far-IR spectral ranges will follow a pixel scheme. The mask function applied to the pulse shaper in order to generate the shaped laser pulses is the direct interface between theory and experiment. Therefore we calculated the mask functions needed to realize our quantum gates and investigated their complexity. The structure of the mask function (transmission and phase) is very simple, and only a few pixels are needed. As an example, the mask function for the CNOT is displayed in Fig. 3. The original pulse to be sent through the pulse shaper (Fig. 3, top) is a 171 fs strictly Fourier limited pulse [center frequency at 674 cm^{-1}, FWHM 590 cm^{-1}, maximum electric field strength 0.0280 a.u. $(2.799 \times 10^{13}\ \mathrm{W/cm^2})$].

The ratios we can achieve with our gates at this stage are rather high, but still below 100%. We have analyzed the losses. Most result from leakage into vibrations that lie outside our chosen Hilbert space and therefore bear little disturbing influence for further calculations. The effect is a diminishing signal when detecting computational results. An estimation shows that at room temperature, normal pressure and an assumed laser focus zone of 200 μm in diameter and 1 cm in length a few hundred quantum gates could be applied successively. This is already enough for some very useful devices (e.g., a quantum factoring engine). We have found that the losses are localized in very few specific vibrational states and can be detected there without disturbing the information stored in our qubit system. Thus error detection is possible in our proposed quantum computing model.

The context of leakage is closely connected to the topic of decoherence. One could think of two different sources of decoherence: resonances between different vibrations (anharmonic resonances and Coriolis coupling) and collisions between molecules. Recent investigations have shown that anharmonic resonances do not cause decoherence at all [19]. Regarding molecules in the gas phase, the number of collisions can be kept low, and typical lifetimes of vibrations are in the nanosecond regime or longer, depending on the experimental conditions. The more significant problem is motion of the molecules within the laser-matter-interaction volume and possibly

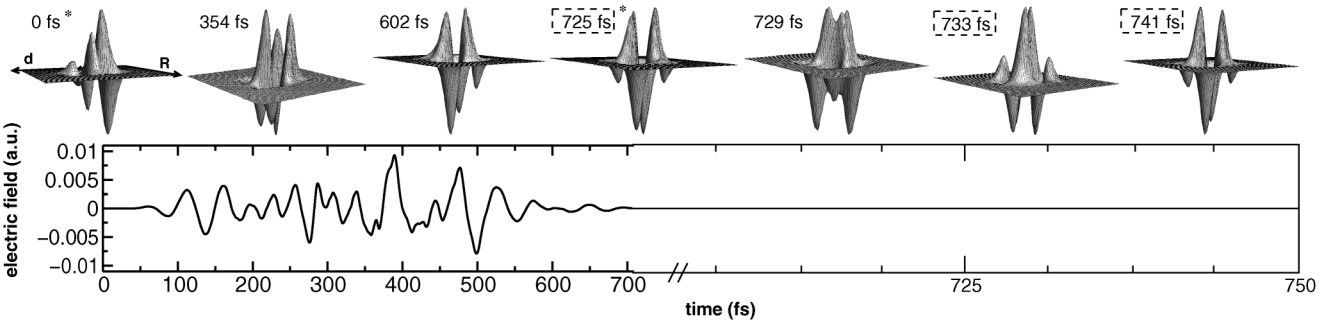

FIG. 2. Preparation of a Bell state: $\frac{1}{\sqrt{2}}[|00\rangle + |10\rangle] \rightarrow \frac{1}{\sqrt{2}}[|00\rangle + |11\rangle]$, efficiency $\geq 98\%$. R is the coordinate of the *cis*-bending mode, d describes the asymmetric CH-stretching mode. Displayed are the laser pulse and the time evolution of the real part of the wave function during the pulse and afterwards. The * indicates the initial and target state; the box labels stay with the same $|\psi|^2$.

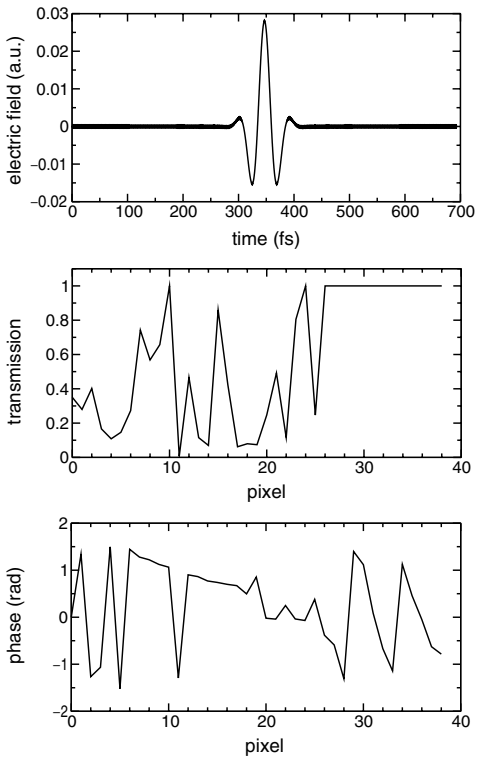

FIG. 3. Mask function for the CNOT gate. For explanation see text.

out of that zone before the next laser pulse is applied. The repetition rate of the lasers is too small and diminishes the number of possible computational steps significantly. These problems can be avoided if fixed molecules are used. One can also think of specially designed macromolecules adsorbed on a surface with the active centers still free to vibrate [22,23] or of molecules embedded in films [24]. Molecular design techniques for self-assembling molecules are well developed at the frontier of nanotechnology [25,26]. Rotations are also suppressed in fixed molecules, and therefore decoherence due to Coriolis coupling is precluded.

In the future, the design of macromolecules consisting of repeated subunits, e.g., subsystems connected through conjugated CC bonds, might play an important role for molecular quantum computing processes. In particular, a collective vibrational mode of all subunits could be used as a data bus in such a quantum network. Every subunit and each vibrational mode has access to the same information coded in the excitation of this collective vibration. An N-atomic macromolecule is an immense qubit system: the number of utilizable qubits scales with 3N, in NMR and ion trap experiments with N.

In summary, vibrationally excited molecules are well suited to implement quantum computation processes. Shaped femtosecond laser pulses act as extremely fast quantum gates and can be designed by applying optimal conrol theory. The calculated laser pulses are simply structured and could be realized in an experimental surrounding where decoherence is negligible.

*Email address: Carmen.Tesch@mpq.mpg.de
†Email address: rdv@mpq.mpg.de

[1] R. Feynman, Int. J. Theor. Phys. **21**, 467 (1982).
[2] D. Deutsch, Proc. R. Soc. London A **400**, 97 (1985).
[3] M. Brune, F. Schmidt-Kaler, A. Maali, J. Dreyer, E. Hagley, J. M. Raimond, and S. Haroche, Phys. Rev. Lett. **76**, 1800 (1996).
[4] J. I. Cirac and P. Zoller, Phys. Rev. Lett. **74**, 4091 (1995).
[5] J. A. Jones and M. Mosca, J. Chem. Phys. **109**, 1648 (1998).
[6] R. Marx, A. F. Fahmy, J. M. Myers, W. Bermel, and S. J. Glaser, Phys. Rev. A **62**, 012310 (2000).
[7] D. J. Tannor and S. A. Rice, J. Chem. Phys. **83**, 5013 (1985).
[8] R. S. Judson and H. Rabitz, Phys. Rev. Lett. **68**, 1500 (1992).
[9] T. Witte, D. Zeidler, K.-L. Kompa, D. Proch, and M. Motzkus, Opt. Lett. (to be published).
[10] R. A. Kaindl, M. Wurm, K. Reimann, P. Hamm, A. M. Weiner, and M. Woerner, J. Opt. Soc. Am. B **17**, 2086 (2000).
[11] C. M. Tesch, K.-L. Kompa, and R. de Vivie-Riedle, Chem. Phys. **267**, 173 (2001).
[12] K. Sundermann and R. de Vivie-Riedle, J. Chem. Phys. **110**, 1896 (1999).
[13] R. Dziewior, K. Romey, and R. Diller, Laser Chem. **19**, 173 (1999).
[14] A. L. Utz, E. M. Carrasquillo, J. D. Tobiason, and F. F. Crim, Chem. Phys. **190**, 311 (1995).
[15] T. Arusi-Parpar, R. P. Schmid, Y. Ganot, I. Bar, and S. Rosenwaks, Chem. Phys. Lett. **287**, 347 (1998).
[16] T. Sleator and H. Weinfurter, Phys. Rev. Lett. **74**, 4087 (1995).
[17] C. M. Tesch, L. Kurtz, and R. de Vivie-Riedle, Chem. Phys. Lett. **343**, 633 (2001).
[18] M. J. Frisch *et al.*, GAUSSIAN98, Revision A.7, Gaussian Inc., Pittsburgh, PA, 1998.
[19] U. Troppmann, C. M. Tesch, and R. de Vivie-Riedle (to be published).
[20] G. van Helden, I. Holleman, M. Putter, A. J. A. van Roij, and G. Meijer, Chem. Phys. Lett. **299**, 171 (1999).
[21] H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K.-L. Kompa, Science **288**, 824 (2000).
[22] G. Meyer, S. Zöphel, and K.-H. Rieder, Appl. Phys. Lett. **69**, 3185 (1996).
[23] S. Mintova and T. Bein, Adv. Mater. **13**, 1880 (2001).
[24] R. Diller, J. Herbst, and K. Heyne, AMOP Frühjahrstagung Osnabrück 2002, SYFS VIII.
[25] E. Mena-Osteritz, A. Meyer, B. M. W. Langeveld-Voss, R. A. J. Janssen, E. W. Meyer, and P. Bäuerle, Angew. Chem. **112**, 2792 (2000).
[26] J. K. Gimzewski and C. Joachim, Science **283**, 168 (1999).