Ultrafast infrared spectroscopy with single molecular ions

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Abstract. We propose a method to investigate the vibrational dynamics of a single polyatomic molecular ion that is co-trapped with an atomic ion. Quantum logic techniques will be used to detect the recoil of a single photon absorption event in the molecule on the atomic ion. This single-molecule recoil spectroscopy can be extended to a pump-probe scheme to investigate ultrafast molecular dynamics. In particular, intra-molecular vibrational dynamics of a single molecular ions can be tracked. We analyze the experimental requirements to investigate the vibrational dynamics in the Cyanoacetylene cation C$_3$HN$^+$.  

1. Introduction

While the quantum state of individual atoms can be manipulated with impressive accuracy [1,2,3], control over single molecules is not as well established [4]. This is due to the complex internal structure of molecules that is rarely suitable for existing state preparation and measurement methods. In particular, direct laser cooling of molecules has proven to be difficult and seems only feasible in a few select molecular species [5,6,4]. For trapped-ion systems, quantum logic techniques have been developed to increase the control over atomic and molecular species that are inaccessible with standard methods [7]. This approach has proven to be useful to enable atomic clocks [7] and also to investigate diatomic molecular ions [8,9,10,11]. Here, we discuss an extension of these methods onto the vibrational degree of freedom of polyatomic molecules.

Existing quantum-logic techniques cannot be easily adapted to the vibrational degree of freedom of molecules as they cannot provide control at the timescale of the molecular dynamics which is usually in the picosecond to femtosecond regime. Coherent control at these timescales can be provided by molecular spectroscopy techniques exploiting ultrafast pulsed lasers [12]. The vibrational structure of complex molecules can be investigated using femtosecond lasers, and the experimental protocols range from simple pump-probe procedures to complex multi-dimensional multi-pulse techniques [12,4].

Here, we consider trapped molecular ions, where most available spectroscopic techniques are destructive and require to dispose of the molecules after each experimental
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implementation [13]. These destructive techniques require a complex experimental setup to sustain a constant flux of molecular ions. For example, electronic transitions of diatomic molecular ions have been investigated with a pump-probe technique by dissociating the molecule and detecting the fluorescence of the remaining atom [14].

In particular, we describe a non-destructive spectroscopic method by combining quantum-logic techniques with ultrafast optical control. In particular, the absorption of a single photon by the molecule is detected via a co-trapped atomic logic ion, a procedure known as recoil spectroscopy [15, 16]. An absorption event comes with momentum kick that alters the combined motional state of both co-trapped particles [15, 16, 17]. The magnitude of the momentum kick from absorbing a single photon is too small to be detected if the motional state of the ion crystal is close to its ground state. It has been shown that single-photon sensitivity can be reached by using a tailored, non-classical, motional state of the trapped particles [15]. Here, we will extend this technique to detect a single-photon absorption event on an infrared vibrational transition in a polyatomic molecule. This detection method can serve as the basis for multiple ultrafast spectroscopic methods.

The separation of timescales of molecular dynamics and atomic control is crucial for the method (as sketched in figure 1) and can be summarized as follows:

- The molecule is irradiated with a single or multiple laser pulses at the femtosecond timescale which leads to energy transfer from the light field to the molecule due to the absorption of photons. Each absorption event leads to an instantaneous change of the momentum of the molecule.
- The Coulomb interaction transfers the momentum kick onto the co-trapped atomic ion. The relevant timescale for the momentum transfer throughout the ion crystal is given by the relevant ion-trap frequency of both ions which is at the microsecond scale.
- The motional state of the atomic ion is mapped onto its electronic state which can be read out with high fidelity at the millisecond timescale.

The proposed quantum logic methods can be applied to a large class of molecules as they rely only on photon absorption which is independent of the internal structure of the molecule. However, the ion trapping environment and other practical consideration limit the set of suitable molecules. Section 2.1 gives an overview over these criteria and discusses possible candidate molecules.

The central method for single-molecule absorption detection is covered in detail in section 2.2. Based on this, a single-pulse absorption ultrafast spectroscopy method is introduced in section 2.3. Such single-pulse schemes show poor spectral resolution, but are a crucial stepping stone towards multi-pulse spectroscopy schemes such as pump-probe spectroscopy and multi-dimensional spectroscopy. In section 2.4, a pump-probe scheme to investigate ultrafast intra-molecular dynamics using quantum logic techniques is introduced. The requirements for a future experimental realization are discussed in section 2.5.
2. Spectroscopic methods

2.1. Relevant molecular properties

The proposed quantum logic methods are mainly independent of the molecular properties but several fundamental and practical considerations limit the set of suitable molecules:

- It should be possible to ionize the molecule without fragmentation and the cation should be stable.

- The molecules should be stable under ion trapping conditions. Electric fields from the trap and the lasers for manipulation and cooling of the atomic logic ion should not dissociate the molecule.

- The ratio between the mass of the molecule and the mass of the atomic logic ion should be within a factor of two. This will allow for efficient sympathetic cooling and the quantum logic readout.

- The molecule should feature vibrational modes that feature a strong infrared transition that is accessible with infrared laser systems. Accessible frequencies lie in the range from $4000 \text{cm}^{-1}$ to $1500 \text{cm}^{-1}$.

In the following, we will introduce the concepts at the example of a specific molecular species, but the techniques can be applied to a wide range of molecules. We will discuss parameter regimes at the example of the Cyanoacetylene cation $C_3HN^+$. This molecule has a mass of 51 dalton and is thus well suited to be co-trapped with $^{40}\text{Ca}^+$, with a mass of 40 dalton. The vibrational modes of the Cyanoacetylene cation have recently been investigated experimentally and theoretically $^{20, 21, 19, 18}$. The vibrational frequencies and intensities are given in table 1. The four stretching modes
Table 1. Experimental and theoretical vibrational frequencies of the Cyanoacetylene cation. Theoretical values have been calculated with restricted open shell DFT calculations at the b3lyp level and a scale factor of 0.97. All values are given in cm$^{-1}$. Values in brackets are IR-intensities in km/mol.

| Mode | Experiment [18] | Experiment [19] | Theory |
|------|-----------------|-----------------|--------|
| $\nu_1$ | 3196.5 (160) | 3123 | 3259 (213) |
| $\nu_2$ | 2175.8 (31) | 2177 | 2206 (2) |
| $\nu_3$ | 1852.8 (372) | 1855 | 1890 (334) |
| $\nu_4$ | - | 829 | 911 (7) |
| $\nu_5$ | - | 648 | 785 (19) |
| $\nu_6$ | - | 422 | 698 (51) |
| $\nu_7$ | - | 203 | 546 (0) |
| $\nu_8$ | - | - | 501 (12) |
| $\nu_9$ | - | - | 220 (0) |

$\nu_1, \nu_2, \nu_3, \nu_4$ feature accessible transition frequencies with calculated transition strengths of 0.21, 0.002 0.34, 0.007 atomic units. These transition strengths have been qualitatively observed in the experiments presented in references [19, 20, 18].

2.2. Single photon absorption detection

In the following, we will introduce a technique to detect a single-photon absorption event via the co-trapped atomic logic ion. We will use a semi-classical description where we treat the light field of the laser classically. For simplicity, we choose a model of the molecule that includes only the ground state and the first excited state of a single vibrational mode. The motion of the two co-trapped particles in a linear ion-crystal will be described by a single-mode harmonic oscillator.

A photon absorption event leads to a recoil with the magnitude of the photon’s momentum $p = \hbar/\lambda$ with $\lambda$ being the wavelength of the photon. The effect of this momentum kick onto the motional mode of the harmonic oscillator can be described by applying a displacement operator onto the motional mode [15]. The magnitude of the displacement is given by the Lamb Dicke parameter $\eta = \sqrt{E_{\text{rec}}/\hbar\omega}$ with the recoil energy $E_{\text{rec}}$ being the photon’s energy and the frequency of the motional mode $\omega$. Absorbing a photon on the molecule exerts thus a momentum kick onto the particle, described by a displacement by the Lamb Dicke parameter $D(\exp(i\phi_s)\eta)$ of the combined motional state of the Coulomb crystal. Here, the angle $\phi_s$ describes the relative phase between the momentum kick and the motion of the harmonic oscillator.

For usual ion trapping conditions and wavelengths in the infrared to visible range, the Lamb Dicke parameter is small ($\eta \ll 1$). If we assume that the crystal is in the motional ground state $|\Psi_{\text{motion}}\rangle = |0\rangle$ then the probability to excite a motional phonon can be approximated by [15]

$$1 - |\langle 0|D(i\eta)|0\rangle|^2 \approx \eta^2.$$
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This represents an upper limit for the probability to detect the absorption event on the logic ion. For a molecule trapped alongside a single $^{40}\text{Ca}^+$ ion the detection probability in the infrared domain is well below $10^{-3}$. This renders the faithful detection of a single absorption event impossible when the initial motional state is the ground state.

It is therefore necessary to increase the detection sensitivity to reach appreciable single-photon detection probability. This can be accomplished by using a state of the harmonic oscillator that is tailored to detect a small displacement. Single-photon sensitivity has been demonstrated in an experiment using an entangled Schrödinger cat state of the motional mode of two distinct atomic species [15]. In this experiment, bichromatic laser pulses were used to generate a non-classical state of the ions’ motion that is also entangled with the electronic degree of freedom. The combined electronic and motional state of the ion can be described as $|\Psi_{\text{ion}}\rangle = |\Psi_{\text{elec}}\rangle \otimes |\Psi_{\text{motion}}\rangle$. The generated Schrödinger cat state is then expressed by

$$
|\Psi_{\text{cat}}\rangle = \frac{1}{\sqrt{2}} \left( |+\rangle_x \otimes |\alpha\rangle + |-\rangle_x \otimes |-\alpha\rangle \right)
$$

where the electronic part is a superposition of the eigenstates of the $\sigma_x$ operator $|\pm\rangle_x$, and the motional part is a superposition of coherent states $|\pm\alpha\rangle$ with displacement $\pm\alpha$.

An absorption of a single photon on the molecular ion will displace the combined motional state of the atom and the molecule by the photon recoil but will not alter the atom’s electronic state. The photon recoil is expressed by a displacement $D(\eta \exp(i\phi_{sc}))$, with the phase $\phi_{sc}$ being determined by the timing of the recoil event relative to the motional mode’s oscillation. The state of the combined system after a recoil event is then

$$
|\Psi'_{\text{cat}}\rangle = \frac{1}{\sqrt{2}} \left( |+\rangle_x \otimes |\alpha + e^{i\phi_{sc}} \eta\rangle + |-\rangle_x \otimes |-\alpha + e^{i\phi_{sc}} \eta\rangle \right).
$$

The photon recoil is then mapped onto the electronic state of the atom by applying a bichromatic light field that implements the inverse state generation operation. After the inverse operation, the displacement from the photon recoil causes a geometric phase of

$$
\theta_g = 2\alpha \eta \sin \phi_{sc}
$$

In analogy to light-force based quantum gates, this geometric phase can be mapped to a bit-flip on the electronic state of the atom in a Ramsey-type experiment [22]. In order to reach the maximum sensitivity of the protocol, the timing of the interrogation laser pulse should be chosen such that $\phi_{sc} = \pi/2$, i.e. the momentum kick is orthogonal to the cat state’s displacement. Then, the probability to detect a single photon absorption on the molecule is

$$
p_{\text{det}} = \sin(2\alpha \eta)^2
$$

For photons that are resonant with the $\nu_3$ transition of Cyanoacetylene, co-trapped with $^{40}\text{Ca}^+$ at a trap frequency of 500kHz, the Lamb Dicke factor will be approximately 0.012. Thus, perfect single-shot detection ($p_{\text{det}} = 1$) of a single-photon absorption event
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needs to satisfy $2\alpha \eta = \pi/2$ and thus a cat state with $\alpha$ of around 70. The cost of increasing the size of the cat state is an increased sensitivity to decoherence effects on the motional mode. Experimentally, the decoherence of the motional mode of the ion crystal is usually limited by motional heating of the ion crystal [23].

The sensitivity of the detection protocol to motional heating has been investigated in reference [15], yielding an error model where the motional decoherence is modeled by random phase fluctuations $\langle \phi^2 \rangle$. These phase fluctuations can be estimated to be

$$\langle \phi^2 \rangle = 8R_h \alpha^2 \frac{2\tau}{3}$$

for a cat-state generation duration $\tau$ and a heating rate $R_h$. The coherence of the Ramsey-like sequence to detect the geometric phase from the photon absorption event is then $C = \exp(-\langle \phi^2 \rangle/2)$.

In order to reach the optimum detection efficiency for a given motional heating rate, one needs to adapt the size of the cat state. The success probability of a single photon absorption event as a function of the cat state displacement $\alpha$ for a state generation duration of $\tau(\alpha) = \alpha \cdot 10\mu$s and multiple motional heating rates is shown in figure 2. It can be seen that for a motional heating rate of around 0.1 quanta/s, a single absorption event can be detected with 60% probability for $\alpha \approx 45$.

\[\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.png}
\caption{Probability to detect a single photon absorption event as a function of the cat state’s displacement $\alpha$ for multiple heating rates of the ion-crystal in the trap. The parameters are for the $\nu_3$ vibration in Cyanoacetylene using a $^{40}$Ca$^+$ logic ion.}
\end{figure}\]

2.3. Single molecule absorption spectroscopy

In the following we will show how the presented quantum logic technique can be used to perform single-molecule absorption spectroscopy in a molecule with multiple vibrational modes. This protocol is intended as a proof of concept rather than a useful spectroscopic technique as its spectral resolution is limited by the Fourier width of the applied ultrafast laser pulse which is usually several terahertz.
We will now consider multiple vibrational modes of the molecule. Thus, we express the state of the molecule as a tensor product of all vibrational modes $|\Psi_{\text{mol}}\rangle = \otimes_j |\nu_j\rangle$ where the state of the mode $j$ is described by $|\nu_j\rangle = \sum_k c_{k,j} |k,j\rangle$, with $c_{k,j}$ the amplitude of the $k$-th excited state of mode $j$. We approximate each mode by a harmonic oscillator, yielding the vibrational Hamiltonian

$$H_{v,0} = \sum_j \omega_j a_j^\dagger a_j$$

with $a_j$ being the annihilation operator of mode $j$ and $\omega_j$ its oscillation frequency. The interaction of the light field $E(t) = E_0 e^{-i\omega_l t}$ with the molecule is then given by the following interaction Hamiltonian:

$$H_I = E(t) \sum_i d_j x_j$$

with $d_j$ the transition moment, and $x_j$ the position operator of the vibrational mode $j$.

Changing the molecule’s state from the ground to an excited state in the mode $j$ comes along with an absorption of a single or multiple photons from the driving laser, each yielding a momentum kick corresponding to a displacement by the Lamb-Dicke parameter $D(i\eta)$. The average number of absorbed photons in mode $j$ is given by the expectation value of the corresponding number operator $a_j^\dagger a_j$. The total momentum change of the motional state $|\Psi_{\text{motion}}(t)\rangle$ is then modeled by applying a displacement only if energy has been transferred into the vibrational mode:

$$|\Psi_{\text{motion}}\rangle = \sum_j N_j \sum_{k=0}^{N_j} \langle k_j | |\Psi_{\text{mol}}\rangle \langle k_j | |\Psi_{\text{mol}}\rangle D(i\eta k) |\Psi_{\text{motion}}\rangle$$

where $|k_j\rangle\langle k_j|$ are the projectors onto the Fock state of mode $j$ with $k$ vibrational quanta. The sum over the vibrational quanta $k$ can be truncated to $N_j$, depending how many excitations can be reached in the mode $j$ constraint by energy conservation. The effect on the motional mode corresponds to a single displacement $D(i\eta)$ operation for every absorbed photon.

As derived in section 2.2, the detection probability on the electronic state of the atomic ion is $p_{\text{single}} = \sin(2\alpha\eta)^2$ for absorbing a single photon. The overall detection probability is then

$$p_{\text{det}} = \sin(2\alpha\eta)^2 \sum_i \sum_k k_i \langle k_i | |\Psi_{\text{mol}}\rangle^2$$

with $|k\rangle$ being a Fock state. Figure 3 shows the expected detection probability on the atomic ion for a Cyanoacetylene ion interrogated with a rectangular 200fs pulse with 100nJ energy focused to a spot of 20µm. The motional cat state had a size of $\alpha = 35$ at a heating rate of 0.2 quanta/s. It can be seen that for the given parameters, the single mode $\nu_3$ can be well isolated.

‡ The wavelength $\eta$ is here the light wavelength, independent of the frequency of the vibrational mode
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2.4. Pump-probe absorption spectroscopy:

In the following we will extend the described single photon absorption detection to investigate vibrational dynamics in a single-molecule using pump-probe spectroscopy. For this, we will again consider the vibrational mode $\nu_3$ of the Cyanoacetylene cation. This transition is accessible with current infrared laser technologies and shows a large dipole moment. We include motional modes $\nu_i$ that do not couple with the light field, but show intra-molecular coupling to the excited mode $\nu_3$. The quantum state of the entire system is described by the state of these modes and the motional state of the ion crystal combined with the electronic state of the atomic ion. The initial state of the system has all vibrational modes in the ground state and the motional state is entangled with the atomic ion’s electronic state by the cat state with displacement $\alpha$. We will express the molecular state by separating the state of $\nu_3$ from the dark modes $\nu$ for clarity:

$$|\Psi_0\rangle = |0, 3\rangle \otimes |\bar{0}\rangle \otimes |\Psi_{\text{cat}}\rangle$$

with the ground state of all dark modes being $|\bar{0}\rangle = \otimes_{j\neq3} |0, j\rangle$.

For pump-probe spectroscopy, two infrared pulses are sent onto the molecule. For simplicity, we assume that the first (pump) pulse of the experiment will prepare the molecule perfectly in the first excited state of the vibrational mode $\nu_3$. Preparing a single vibrational mode in the excited state with high fidelity with a laser pulse at the femtosecond timescale has been demonstrated in multiple molecular systems with a temporal pulse shape that is tailored to the molecule using optimal control techniques [24]. If the preparation cannot be performed with high fidelity, the detection efficiency will be reduced, but the method can still be applied.

The pump pulse induces a single vibrational quantum in $\nu_3$ and corresponds thus to a single photon absorption event, displacing the the motional state of the ion-crystal:

$$|\Psi_{\text{pump}}\rangle = |1, 3\rangle |\bar{0}\rangle \otimes D(i\eta)|\Psi_{\text{cat}}\rangle$$

where the motional state has been displaced due to the photon recoil.
The system is then subject to a free evolution with time $t$. During this time, the vibrational excitation will be redistributed over the modes $\tilde{\nu}_k$, yielding the state

$$|\Psi_{\text{evol}}\rangle = \sum_m c_m(t)|\nu_{3,m}\rangle \otimes |\tilde{\nu}_m\rangle \otimes D(i\eta)|\Psi_{\text{cat}}\rangle$$

where the molecular state is now in a superposition of multiple vibrational modes, expressed by $\sum_m c_m(t)|\nu_{3,m}\rangle \otimes |\tilde{\nu}_m\rangle$.

Then, a second (probe) pulse is applied onto the molecule, aiming to undo the pump pulse, de-exciting the mode $\nu_3$. For the part of the state, where no energy has been transferred ($\nu_3$ is still in the excited state $|1,3\rangle$), the pulse de-excites the vibrational mode into the ground state. This de-excitation comes along with the stimulated emission of a photon which causes a displacement with opposite sign relative to the pump pulse $D(-i\eta)$. For the part of the state where the energy has been transferred to a dark mode (and thus the $\nu_3$ mode is in its ground state $|0,3\rangle$), the probe pulse will excite the $\nu_3$ mode, introducing energy to the system and causing a displacement that is in phase with the displacement caused by the pump pulse $D(i\eta)$.

The state of the system after the probe pulse is given by

$$|\Psi_{\text{probe}}\rangle = c_0(t)|1,3\rangle \otimes |\tilde{0}\rangle \otimes |\Psi_{\text{cat}}\rangle + \sum_m \tilde{c}_m(t)|0,3\rangle \otimes |\tilde{\nu}_m\rangle \otimes D(2i\eta)|\Psi_{\text{cat}}\rangle$$

where $|\tilde{\nu}_m\rangle$ is a basis of the excited dark states. The exciting and de-exciting momentum kicks cancel each other on the part of the population where the vibrational excitation remains in the $\nu_3$ mode expressed by the amplitude $\nu_3(t)$. For the other parts of the state, the momentum kicks add coherently, resulting in a larger displacement of $D(2i\eta)$.

By detecting the displacement after both pulses with the method outlined in section 2.2 one can measure the loss of population from the $\nu_3$ mode to the dark modes $\tilde{\nu}$. The cancellation of the momentum kicks relies on the fact that the displacement operations caused by the pump pulse and the probe pulse have opposite phases. This assumption is only valid if the harmonic oscillator of the motional state does not evolve in the time between the pump and the probe pulses. In typical molecular systems, the vibrational dynamics occurs at the picosecond timescale scale which is small compared to the oscillation period of the ion crystal in the microsecond range.

We will now discuss the expected outcome of the pump-probe methods for simple models of relaxation processes of the excited vibrational mode. First, we will consider relaxation into multiple rotational and vibrational states that act as a continuous bath of modes. Such processes are known as incoherent intramolecular vibrational relaxation (IVR) and can be described by an exponential decay of the original mode to other modes without any coherent revivals [25]. To our knowledge, the IVR timescale for the Cyanoacetylene cation has not been measured and thus we approximate it with the decay in neutral Cyanoacetylene, which has been measured to be 26ps [26]. The expected outcome of a pump-probe experiment when incoherent IVR processes dominate the relaxation is shown in figure 4.
Another type of IVR features coherent transfer to other vibrational modes \[25\]. To model such a transfer in Cyanoacetylene one needs to consider an anharmonic model of the molecule which allows coupling between modes with different mode frequencies. In this first-order model, significant coupling occurs only between vibrational states that show a frequency mismatch that is in the order of the coupling strength between them \[27\]. Thus, one can define subspaces of states that show small frequency mismatch and couple to each other, yielding a block-diagonal coupling Hamiltonian in the \( |j, i\rangle \) basis \[27\].

The pump pulse prepares the Cyanoacetylene molecule in the \( |1, 3\rangle \) state. We will consider coupling to the \( |2, 4\rangle \) state which has the smallest detuning to the prepared state of \( \Delta = 2\nu_4 - \nu_3 = 68\text{cm}^{-1} \). The coupling strength between the modes is not known for the Cyanoacetylene cation and thus we approximate them with \( g = 30\text{cm}^{-1} \), a typical coupling strength between vibrational modes in acetylene \[26\]. This leads to dynamics showing a partial oscillation of the excitation between the two modes, which is damped by the incoherent IVR process as described above. The expected measurement signal for pump and probe pulses that enable full state transfer is shown in figure 4. It should be noted here, that the simple IVR model neglects rotational effects which will damp the oscillation considerably \[27\].

![Figure 4](image-url)

**Figure 4.** Expected measurement signal for a pump-probe experiment on the \( \nu_3 \) mode of Cyanoacetylene where incoherent IVR processes (blue) and coherent coupling between two vibrational modes (orange) are dominant. Parameters for the figure are \( \alpha \approx 25 \) and a heating rate of 0.2 quanta/s.

2.5. The experimental platform

In the following, we will discuss the requirements for an experimental system capable of implementing the proposed schemes.

For the proposed methods, excellent coherent control over the motion of a two-ion crystal needs to be provided. For this task, a macroscopic linear quadrupole ion trap is a natural choice due to its large ion-surface distance that will enable low motional heating rates. A low heating rate is crucial for the proposed experiments as it is expected
that the efficiency of detecting a single photon absorption event will be limited by the motional heating rate \[15\]. Heating rates below one quantum/s have been observed in macroscopic traps with electrode-ion distance in the millimeter range \[23\]. It is expected that the motional coherence can be increased by more than one order of magnitude when cooling the trap to 70K, as it is known that the surface processes that lead to excessive motional heating are suppressed at low temperatures \[23\]. Thus, a macroscopic linear trap at a temperature of 70K should have a heating rate of significantly less than 1 quanta/s to enable single-shot single-photon absorption detection.

![Figure 5. Sketch of the experimental setup, including logic-ion laser system and the molecular optical control system.](image)

The choice of atomic ion determines a suitable mass range for the investigated molecules. A suitable atomic ion species of choice is \(^{40}\text{Ca}^+\), as it allows one to sympathetically cool molecules with masses ranging from around 30 to 100 dalton \[10\]. This species has the additional advantage that the wavelengths of the required lasers are all above 395nm, which usually does not dissociate the molecules of interest.

The molecule needs to be ionized inside the trapping volume of the trap where the logic ion is already trapped. This can be achieved, by injecting the molecules that are in the gas phase into the vacuum vessel. The molecule will be immediately cooled by the logic ion after the ionization which leads to the formation of a Coulomb crystal which can be detected by a change in position of the logic-ion. Robust molecules can be readily ionized by electron bombardment, whereas for more complex and fragile molecules photo-ionization is the technique of choice.

Control over the molecule’s vibration will be provided by an infrared ultrafast femtosecond laser system. The laser system needs a sufficiently high light intensity to perform the pumping step with a single laser pulse on the \(\nu_3\) vibrational mode. If we assume a pulse energy of 600nJ, yielding a peak laser power of \(3 \cdot 10^6\)W. The laser can be focused to a spot size of 10\(\mu\)m using a NA=0.2 objective, resulting in a Rabi frequency of approximately \(2\pi \cdot 4 \cdot 10^{13}\)Hz, which should be sufficient to perform a pulse that transfers all population into the first excited state of the vibrational mode \(\nu_3\).

Such a laser system is commercially available using a high power fiber based master
oscillator and an optical parametric amplifier. Such a system will produce laser pulses at wavelengths ranging from 3\(\mu\)m to 10\(\mu\)m with a duration of 200fs and a single pulse energy ranging from 800nJ to 200nJ. The repetition rate of the system is 1MHz which can be synchronized with the frequency of the motional mode of the trapped ions in order to maximize the acquired geometrical phase in the absorption detection protocol.

The spectrum of the pulses can be manipulated using a pulse shaper based on a spatial light modulator. Single pulses can be selected using an acousto-optical modulator. A sketch of the proposed system is shown in figure 5.

3. Discussion and outlook

We have introduced non-destructive methods to perform ultrafast spectroscopic techniques on single molecular ions using quantum logic readout with a co-trapped atomic ion. We anticipate that a single photon absorption event can be detected with a probability of 60% using realistic experimental parameters. This absorption detection is the basis for a pump-probe technique that will give insight into intramolecular dynamics of single molecular ions.

Within this manuscript we have deliberately chosen a simple model of the molecule to emphasize the basic working principle. We will briefly discuss the expected impact of a more complex molecular model including additional degrees of freedom:

- Rotational degree of freedom: The rotational degree of freedom of the molecules has been neglected in the light-molecule interaction. This approximation is justified because the laser pulses are usually in the femtosecond timescale and rotational dynamics of polyatomic molecules occurs in the picosecond to nanosecond domain. Thus, rotational effects will play a role when investigating the time dynamics of the vibrational modes but will not affect the spectroscopic technique itself. The pump-probe experiments are expected to show dephasing and rephasing dynamics as have been observed in ultrafast experiments [4].

- Anharmonic nature of the vibrational modes: To describe the vibrational dynamics in molecules it is often necessary to describe the vibrational modes by anharmonic oscillators. Due to this anharmonicity, the oscillators can be excited at integer multiples of their fundamental oscillation frequency. This leads to denser infrared spectra and additional coupling between vibrational modes. However, the light-molecule interaction and thus the spectroscopic technique should be unaffected by such anharmonic effects.

- Spin-orbit coupling and Zeeman substructure: For the investigated Cyanoacetylene molecule, the spin-orbit coupling is much smaller than the spectral width of the exciting femtosecond laser pulses [19]. Thus, this substructure cannot be resolved and can thus be neglected for the light-molecule interaction.

The presented methods are stepping stones towards more complex spectroscopic schemes. Existing spectroscopic methods can be straightforwardly transferred using
the presented absorption detection. The measured quantity with the quantum logic technique is the net recoil that all laser pulses excerpt onto the molecule and thus the interpretation of the experimental outcomes needs to be adapted.

The amount of extracted information from the molecule can be increased by exploiting multiple modes of the motion of the ion crystal. This will enable to measure correlations between the pathway and the final state of intramolecular processes on a single-molecule and single-shot level. For example, one mode can be used to measure the final state of the dynamics and the second mode can be used to distinguish distinct pathways of intramolecular dynamics.
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[1] P. Schindler, D. Nigg, T. Monz, J. T. Barreiro, E. Martinez, S. X. Wang, S. Quint, M. F. Brandl, V. Nebendahl, C. F. Roos, M. Chwalla, M. Hennrich, and R. Blatt, “A quantum information processor with trapped ions,” New Journal of Physics, vol. 15, p. 123012, aug 2013.

[2] D. Wineland, “Experimental Issues in Coherent Quantum-State Manipulation of Trapped Atomic Ions,” Journal of Research of the National Institute of Standards and Technology, vol. 103, 1998.

[3] R. Grimm, M. Weidemüller, and Y. B. Ovchinnikov, “Optical dipole traps for neutral atoms,” Advances In Atomic, Molecular, and Optical Physics Volume 42. Series: Advances In Atomic, Molecular, and Optical Physics, ISBN: 9780120038428. Elsevier, vol. 42, pp. 95–170, feb 1999.

[4] M. Lemeshko, R. V. Krems, J. M. Doyle, and S. Kais, “Manipulation of molecules with electromagnetic fields,” Molecular Physics, vol. 111, no. 12-13, pp. 1648–1682, 2013.

[5] D. W. Chandler and K. E. Strecker, “The quest for cold and ultracold molecules,” ChemPhysChem, vol. 10, no. 5, pp. 751–754, 2009.

[6] E. S. Shuman, J. F. Barry, and D. Demille, “Laser cooling of a diatomic molecule,” Nature, vol. 467, pp. 820–3, oct 2010.

[7] P. O. Schmidt, T. Rosenband, C. Langer, W. M. Itano, J. C. Bergquist, and D. J. Wineland, “Spectroscopy using quantum logic,” Science, vol. 309, pp. 749–52, jul 2005.

[8] C.-w. Chou, C. Kurz, D. B. Hume, P. N. Plessow, D. R. Leibrandt, and D. Leibfried, “Preparation and coherent manipulation of pure quantum states of a single molecular ion,” Nature, vol. 545, no. 7653, pp. 203–207, 2016.

[9] F. Wolf, Y. Wan, J. C. Heip, F. Gebert, C. Shi, and P. O. Schmidt, “Non-destructive state detection for quantum logic spectroscopy of molecular ions,” Nature, vol. 530, pp. 457–460, feb 2016.

[10] D. Leibfried, “Quantum state preparation and control of single molecular ions,” New Journal of Physics, vol. 14, p. 023029, 2012.

[11] S. Ding and D. N. Matsukevich, “Quantum logic for the control and manipulation of molecular ions using a frequency comb,” New Journal of Physics, vol. 14, p. 023028, 2012.

[12] D. Brinks, R. Hildner, E. M. H. P. van Dijk, F. D. Stefani, J. B. Nieder, J. Hernando, and N. F. van Hulst, “Ultrafast dynamics of single molecules,” Chemical Society Reviews, vol. 43, no. 8, p. 2476, 2014.

[13] S. Willitsch, “Chemistry With Controlled Ions,” in Advances in Chemical Physics, pp. 307–340, Wiley-Blackwell, oct 2017.

[14] S. Kahra, G. Leschhorn, M. Kowalewski, A. Schiffrin, E. Bothschafter, W. Fuß, R. de Vivier-Riedle, R. Ernstorfer, F. Krausz, R. Kienberger, and T. Schaetz, “A molecular conveyor belt by controlled delivery of single molecules into ultrashort laser pulses,” Nature Physics, vol. 8, no. 3, pp. 238–242, 2012.

[15] C. Hempel, B. P. Lanyon, P. Jurcevic, R. Gerritsma, R. Blatt, and C. F. Roos, “Entanglement-enhanced detection of single-photon scattering events,” Nature Photonics, vol. 7, pp. 630–633, apr 2013.

[16] Y. Wan, F. Gebert, J. B. Wübbena, N. Scharnhorst, S. Amairi, I. D. Leroux, B. Hemmerling, N. Lörch, K. Hammerer, and P. O. Schmidt, “Precision spectroscopy by photon-recoil signal amplification,” Nature communications, vol. 5, p. 3096, 2014.

[17] C. R. Clark, J. E. Goeders, Y. K. Dodia, C. R. Viteri, and K. R. Brown, “Detection of single-ion spectra by Coulomb-crystal heating,” Physical Review A, vol. 81, p. 043428, apr 2010.

[18] A. M. Smith-Gicklhorn, M. Lorencz, R. Kolos, and V. E. Bondybey, “Vibrational spectroscopy of matrix-isolated, mass-selected cyanoacetylene cations,” Journal of Chemical Physics, vol. 115, no. 16, pp. 7534–7542, 2001.

[19] A. Desrier, C. Romanzin, N. Lamarre, C. Alcaraz, B. Gans, D. Gauyacq, J. Lievin, and S. Boye-Peronne, “Experimental and ab initio characterization of HC3N+ vibronic structure. I. Synchrotron-based threshold photo-electron spectroscopy,” Journal of Chemical Physics, vol. 145, no. 23, pp. 0–16, 2016.

[20] Z. Dai, W. Sun, J. Wang, and Y. Mo, “The Renner-Teller effect in HCCC(N+(XΣf/2I)) studied
by zero-kinetic energy photoelectron spectroscopy and theoretical calculations,” *The Journal of Chemical Physics*, vol. 143, p. 054301, Aug 2015.

[21] P. Botschwina, “A theoretical investigation of HC3NH+,” *Chemical Physics Letters*, vol. 139, no. 3, pp. 255–261, 1987.

[22] A. Sørensen and K. Mølmer, “Quantum Computation with Ions in Thermal Motion,” *Physical Review Letters*, vol. 82, no. 9, pp. 1971–1974, 1999.

[23] M. Brownmuntt, M. Kumph, P. Rabl, and R. Blatt, “Ion-trap measurements of electric-field noise near surfaces,” *Reviews of Modern Physics*, vol. 87, p. 1419, Sep 2015.

[24] E. Berrios, M. Gruebele, D. Shyshlov, L. Wang, and D. Babikov, “High fidelity quantum gates with vibrational qubits,” *Journal of Physical Chemistry A*, vol. 116, no. 46, pp. 11347–11354, 2012.

[25] A. H. Zewail, “IVR: Its Coherent and Incoherent Dynamics,” *Berichte der Bunsengesellschaft für physikalische Chemie*, vol. 89, no. 3, pp. 264–270, 1985.

[26] A. Kushnarenko, *Investigation of intramolecular vibrational energy flow in polyatomic molecules by the femtosecond pump-probe technique*. PhD thesis, ETH Zurich, 2013.

[27] M. Gruebele, “Mechanism and control of molecular energy flow: a modeling perspective,” *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)*, vol. 109, pp. 53–63, Mar 2003.