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Nondestructive inelastic recoil spectroscopy of a single molecular ion: A versatile tool toward precision action spectroscopy

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We demonstrate a single-molecule technique that is compatible with high-precision measurements and obtain the spectrum of three molecular ion species. While the current result yields a modest spectral resolution due to a broad light source, we expect the method to ultimately provide a resolution comparable to quantum logic methods with significantly less stringent requirements. Adaptations of this technique will prove useful in a wide range of precision spectroscopy arenas including the search for parity-violating effects in chiral molecules.

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Ion traps present a powerful platform for precision spectroscopy of molecular ions. In particular, molecular spectroscopy in mixed-species Coulomb crystals, composed of a molecular ion and laser-cooled atomic ion, affords a level of exceptional molecular control that in turn leads to long interrogation times [1] and unparalleled spectroscopic resolution [2]. These techniques are actively investigated for applications in testing fundamental physics [3], *ab initio* theory [4], cold reactions [5,6], and chemical dynamics [7–9]. Within this framework, nondestructive quantum logic spectroscopy (QLS) techniques have emerged as the gold standard for precision spectroscopy of a single molecular ion [10]. These methods coherently drive molecule-atom pair translational motion in the trap in a state-specific way, and provide nondestructive amplification of a transition measurement. Despite significant strides in recent years, quantum logic techniques remain technically challenging and have yet to be implemented on a polyatomic molecule.

In contrast, action spectroscopy is a versatile and diverse framework for obtaining the spectra of molecular ions ranging from simple diatomics to large biomolecules [11]. Tagging spectroscopy, a form of action spectroscopy, weakly adheres an inert gas “tag” such as a noble gas atom or N_2 via a van der Waals interaction with the molecule. Resonant excitation of the vibrational modes of the molecule detaches the tag and is detected as a change in mass of the complex [12]. Action spectroscopy in laser-cooled Coulomb crystals has been largely limited to destructive photodissociation measurements [13,14], although a tagging spectrum of single molecular ions was recently demonstrated [15]. The lifetime-limited resolution of tagging and photodissociation methods have led to the search for less perturbative methods [16,17]. Schmid *et al.* recently demonstrated leak-out spectroscopy, a method which has been used to record high-resolution rovibrational spectra of a wide range of molecular ions [18,19]. The technique takes advantage of inelastic collisions between vibrationally excited molecular ions and cold buffer gas atoms or molecules. These collisions internally cool the molecular ions while simultaneously imparting a large (∼10 meV) kinetic energy recoil to the molecule. This kinetic energy is sufficient to eject the molecular ion from the trap, where it is detected. This method yields a spectral resolution of ∼MHz, set by the first-order Doppler width of the cold (∼15 K) molecular ions. Our method, inelastic recoil spectroscopy (IRS), extends leak-out spectroscopy to nondestructively record the spectra of single, Coulomb-crystallized molecular ions.

We demonstrate IRS and record the vibrational spectra of a single tropylium (Tr^+, $C_7H_7{}^+$) molecule, a single benzodioxol fragment (Bd^+, $C_7H_5O_2{}^+$) molecule, and a single protonated diacetylene (PD^+, $C_4H_3{}^+$) molecule. The molecule of interest is cotrapped with a laser-cooled $^{88}Sr^+$ atomic ion, and inelastic collisions are detected nondestructively via observation of the $^{88}Sr^+$ fluorescence. Thus, our method retains the generality of the leak-out spectroscopy technique, but allows for spectroscopy to be performed on highly controlled single molecular ions, as in QLS. Future experiments can be performed in the Lamb-Dicke regime, which is immune to first-order Doppler shifts. This combination of generality and precision suggests the method will represent a significant contribution to the molecular spectroscopy tool suite.

Our apparatus is a slightly modified version of the apparatus used to obtain the tagging spectrum of single molecular ions [15,20], shown in Fig. 1(a). A linear quadrupole Paul trap is enclosed in a 7-K copper shield, and can be mass-selectively loaded with $^{88}Sr^+$ ions and molecular ions as in Ref. [20]. We load a single molecular ion and a small number (1–3) of $^{88}Sr^+$ atoms. The mixed-species ensemble is laser cooled into a Coulomb crystal via Doppler cooling on the $5S_{1/2} \rightarrow 5P_{1/2}$ 422-nm transition in $^{88}Sr^+$ (Doppler temperature ∼300 μK). The ensemble is exposed to low-pressure He gas at ∼8 K. Based on the time (∼100 ms) between $^{88}Sr^+$ - molc.$^+$ ↔ molc.$^+$ - $^{88}Sr^+$ reorganization events, we estimate a He pressure on the order of 10^{-8} Torr [20]. This estimate is consistent with the base pressure reading of 3×10^{-8} Torr from an ion gauge that measures the pressure of the room-temperature

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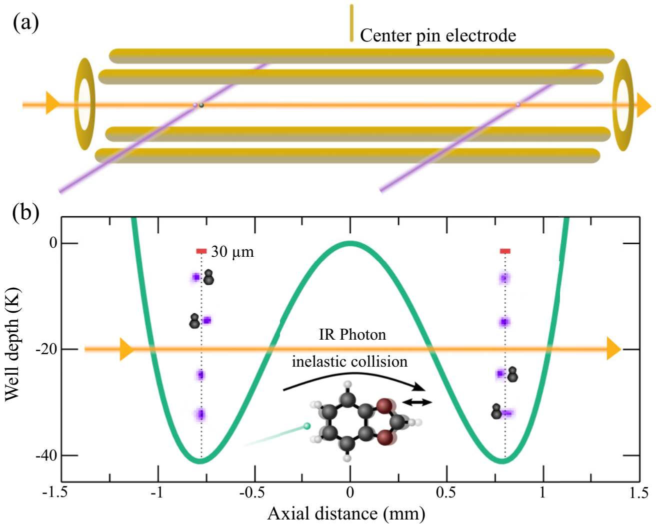

FIG. 1. (a) A schematic of the trap (not to scale) shows the layout of the center pin relative to the rest of the linear Paul trap. Details of the trap are described in Ref. [20]. Two radial cooling beams (violet) are aligned to laser cool $^{88}Sr^+$ in each well. The mid-IR OPO (orange) is aligned along the trap axis with an axial cooling beam (not shown). (b) The estimated double-well potential along the axial direction of the trap is shown. The false-colored violet spots represent $^{88}Sr^+$ ions isolated from a series of four frames taken with a camera imaging both wells. The molecule is represented by a space-filling cartoon with a dotted guide added to highlight the single-ion trap position for each well. In this case, a Bd^+ molecular ion flips to the right well between the second and third frames, following a 500 ms exposure to the mid-IR OPO on resonance with a dipole-allowed C-H stretch mode and an inelastic collision with He. The 30 μm distance between ions in the frame is estimated from the measured axial secular frequency.

dewar that contains the cryocooled trap. Collisions with this gas serve to rotationally cool the molecule, but are not sufficient to melt the Coulomb crystal. C-H stretch modes of the molecular ion are excited with a mid-IR (3030 cm^{-1}) optical parametric oscillator (OPO). As in Refs. [18,19], we rely on inelastic collisions of a vibrationally excited molecule with a cold (8-K) buffer gas particle, typically He. For a vibrational excitation of Tr^+ at 3030 cm^{-1}, a quenching resulting from the inelastic collision distributes the 375 meV (4350 K) between the vibrational and rotational degrees of freedom for the molecule as well as translational energy for both collision partners. A kinetic energy of about 16 meV (183 K) imparted on the molecular ion is enough to substantially reorganize the configuration of atomic and molecular ions in the trap whereas elastic collisions of 8 K He do not. The relatively large energy scales of the inelastic recoil makes ground state cooling unnecessary, at the cost of quantum state preparation as is realized in QLS. The locations of the molecular ion are inferred from the position of the atomic ions imaged using laser-induced fluorescence.

We demonstrate IRS in two distinct configurations. In the *double-well configuration*, the molecular ion is held in one of two wells, with a barrier chosen such that the inelastic recoil is sufficient to cross between two trapping regions. In the *single-well configuration*, the inelastic collision momentarily knocks the molecular ion out of a two-ion crystallized configuration, allowing the atomic ion to occupy the trap center. The ion positions are monitored by an electron-multiplying charge-coupled device (EMCCD) (Q Imaging Retiga R1) from both the side and from below the ion trap. A portion (70%) of the fluorescence from the bottom is sent to a photomultiplier tube (PMT) to enable the measurement of the axial secular frequency via Doppler-modulated fluorescence [20]. The axial secular frequency is used to confirm the mass of a cotrapped molecular ion [21], determine the distance between ions [22], and detect recoil events.

To realize the double-well trap shown in Fig. 1, an additional center pin electrode was added 4 mm above the trap center. When no voltage is applied to this center pin, the trap has a single well. Both the desired molecular ion and $^{88}Sr^+$ are trapped initially in the single-well configuration. A voltage is applied to the center pin electrode and the trap is recompensated [23] to produce the double-well potential. We typically observe bifurcation around 65 V on the center pin electrode. The center pin voltage is raised further to 75–80 V to minimize the background flipping events where ions change position between the left and right well. We find this barrier height is sufficiently low to allow the molecule to flip between wells during inelastic collisions. We also find that the trap should be reasonably well compensated to prevent background flipping events, presumably during energetic collisions activated by the micromotion. The axial double-well potential, determined by the locations of the minima and the secular frequencies within each well, is shown in Fig. 1.

We estimate the barrier height around 40 ± 10 K. This height is large compared to the laser-cooled motional temperature of the mixed-species crystal, but small compared to the recoil energy from a vibrational-quenching transition. Without laser cooling, the ion temperature quickly warms to ~8 K via elastic collisions with background gas, which is sufficient to reshuffle the ions between wells. We indeed observe that both atomic and molecular ions reshuffle between the two wells at random when the cooling light is momentarily blocked.

During an experimental cycle, a single molecular ion is cotrapped with one or two atomic ions in the left well of the double trap. The atomic ions provide sympathetic cooling to millikelvin temperatures as well as providing a visual confirmation of the presence of the molecular ion. A single $^{88}Sr^+$ is trapped in the right trapping region to provide confirmation of a flip event. A mechanical shutter opens to expose the molecular ion to a mid-IR OPO beam coaligned with the axial cooling beam. The total exposure time before the molecular ion flips to the right potential well is recorded and used to estimate a flipping rate. A total of six data points at each wavelength step was used to obtain the spectra in Fig. 2. After recording a molecule flipping event, the configuration is reshuffled as necessary.

The spectra in Fig. 2 demonstrate the double-well configuration of IRS with two molecular ions previously studied using tagging spectroscopy with N_2 [15,20]. The tag perturbs vibrational energies on the order of a few cm^{-1} [24,25], with the shift observed in the IRS spectrum compared to previous tagging experiments indicating that the IRS method does measure the bare molecular ion. The lifetime limit for the

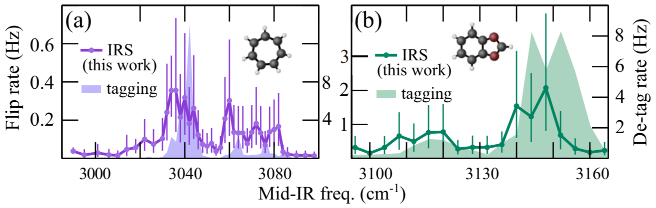

FIG. 2. The inelastic recoil spectra for Tr^+ and Bd^+ are shown with a maximum-likelihood estimate of the rate with error bars at the 95% confidence interval (see Refs. [15,20]). Both spectra are in agreement with the spectra taken by tagging the respective molecule shifted by 4.5 cm^{-1}. Error bars on the tagging spectra are suppressed for clarity.

van der Waals complex used in tagging spectroscopy imposes a resolution limit from ∼10 GHz to 10 THz [26]. Without this large lifetime limit, IRS should fully rotationally resolve molecular spectra with a suitably narrow mid-IR source.

Although the double-well method robustly produces spectra, a single-well measurement is preferable as a more straightforward approach with a faster data acquisition cycle. As a proof of concept, we implement one possible strategy using lock-in detection as shown in Fig. 3. An inelastic recoil event knocks the molecular ion out of the trap null allowing the $^{88}Sr^+$ to return to the single-ion center position. A constantly applied tickle at the single $^{88}Sr^+$ secular frequency amplifies the secular motion and Doppler-modulates the fluorescence. The Doppler modulation is detected by lock-in as an increase in the lock-in R value and the proportional time above a predetermined threshold is recorded. We demonstrate the single-well method on the astrochemically relevant PD^+ [27,28] produced from the 51-Da fragment from electron impact-ionized benzaldehyde. The resulting spectrum agrees well with *ab initio* predictions for this molecule.

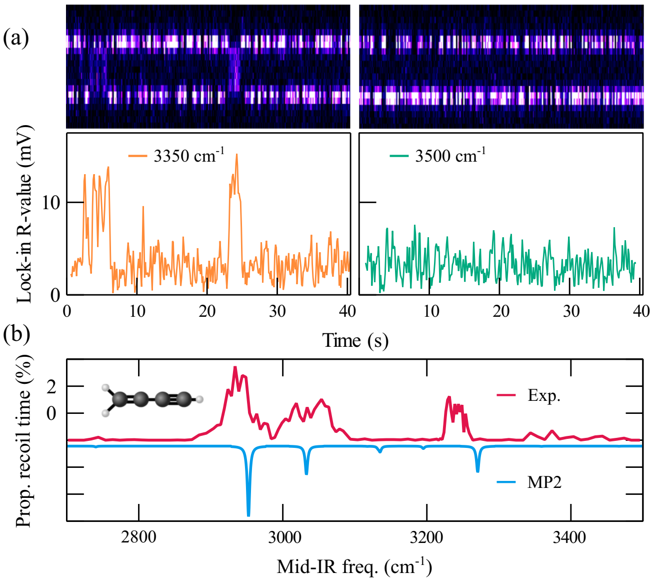

FIG. 3. (a) Collated frames (200 ms each) of PD^+ and $^{88}Sr^+$ exposed to mid-IR near a weak resonance (3350 cm^{-1}) and off resonance (3500 cm^{-1}) show inelastic ejection events correspond to an increase in the lock-in R value (integration time of 100 ms) locked to the single $^{88}Sr^+$ secular frequency. (b) The duration that the crystal configuration lock-in R value exceeds the 10 mV threshold is normalized to the total 120 s exposure to the mid-IR source for each frequency step. The resulting spectrum agrees with transitions predicted based on normal mode energy calculations using second order Møller Plesset perturbation theory with the AUG-cc-pVTZ basis set. Anharmonic second order perturbation theory corrections were made using the GVPT2 generalized vibrational perturbation theory to second order (GVPT2) model.

This platform of action spectroscopy extends leak-out methods into the regime of indefinite trapping time as the molecule is retained in the trap during measurement. Inelastic collisions with background buffer gas are intrinsically inefficient. Although increasing the background collision rate (e.g., the pressure) seems like a natural choice, saturation has been observed as the vibrationally quenched molecule is rethermalized by subsequent collisions on timescales faster than the detection [29]. The long interrogation time in this setup allows the extraction of a signal even when the rate coefficient for vibrational quenching is low without requiring higher background gas pressure. We have demonstrated nondestructive IRS on molecules as massive as 121 Da. Simple modifications of the method may extend the range of masses accessible. For example, a mass-dependent parametric tickle [30] could of the molecule's radial secular frequency could be used to amplify the excursion of the molecular ion from the trap null caused by a recoil event or the axial confinement could be modified to slow the sympathetic recooling rate.

The low motional temperature and highly controlled environment of a single trapped ion presents an attractive staging ground for precision measurement. In particular, tightly confined ions can be interrogated in the Lamb-Dicke regime [31], which is free of the first-order Doppler effect [32,33]. The work presented here was done with a rather low-resolution (∼6 cm^{-1}, 0.18 THz linewidth) widely tunable light source, but the resolution of a future experiment with a narrow spectroscopy laser would be limited only by the natural linewidth of the probed transition, the second-order Doppler effect, and collisional broadening. All contributions are estimated at $\lesssim$100 Hz. Such an experiment would easily resolve rotational lines. In a rotationally resolved experiment, background gas collisions would cycle the molecule through rotational states until it lands in the probed state and is subsequently vibrationally excited [18].

The ability to resolve rotational lines, in combination with microwave-mediated enantiomer-specific state transfer, would enable the nondestructive determination of the chirality of a single, trapped molecular ion [34–36]. Chiral molecular ions are proposed as promising candidates for observation of small parity nonconservation (PNC) effects [37]. An extension of this IRS method toward ultrahigh-resolution spectroscopy with a suitably narrow laser source [38] presents a promising avenue for observing the effect in molecules, with no requirement to synthesize an enantiopure sample.

In addition to the possibility of measuring PNC effects, the method presents applications in studying molecules of astrophysical interest. Molecular ions are suspected to play an important role in astrochemistry, but the low density of molecular ions makes obtaining spectra with sufficient resolution challenging. The enhanced sensitivity of action techniques such as tagging have resulted in the heralded identification of $C_{60}{}^{+}$ in the interstellar medium [39]. Tagging spectroscopy, even with an "innocent" tag such as He, can shift the vibrational spectra of the observed complex relative to the bare molecule and requires careful understanding of these perturbations [40]. A spectroscopic method that measures the bare molecular ion is therefore invaluable for astrophysical determination. The long lifetime of a molecular ion in the trap may allow the creation of understudied reactive species via chemical or photofragmentation processes with low formation rates to compliment progress toward this goal [41]. Further purification to remove different chemical or isomeric species' contributions to the spectra is not required due to the innate purity of a single molecule.

The nondestructive nature of detection presents an intriguing method for analysis of extremely costly samples. Future refinements of this apparatus with enhanced loading efficiency could find use in the identification of molecules of possible biological origin on Enceladus [42], Titan [43,44], and Europa.

In conclusion, we have demonstrated a general method for performing vibrational spectroscopy on single molecular ions. Straightforward extensions of the technique are expected to yield ultraprecise molecular spectroscopy, single-molecule chiral readout, and an unambiguous single-molecule method for general chemical analysis.

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