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Thermally activated hopping of two ions trapped in a bistable potential well

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Abstract
With two ions in a spheroidal Paul trap, the harmonic trapping potential turns, by Coulomb repulsion, into a *bistable* well. Two Ba ions have been confined, laser-cooled, and observed, via their laser-excited resonance scattering, by a spatially resolving photomultiplier, or intensifying CCD camera. A repump laser releases the ions from a metastable state. Well-cooled ions are found localized. When the laser is detuned, the Raman cooling rate and the ions' temperature vary. A transition from the crystallized state to a toroidal gas takes place.

The ions are discriminated when one (i) gets excited into a non-fluorescing metastable state, or (ii) is of another isotopic species. Hopping rates of 1 s^{-1} are found at high thermal excitation. Elsewhere, the rates drop by two orders of magnitude, and vary resonantly with temperature near potential energy/kinetic energy = 15, where the bright ion's hopping upstream of the laser beam is five times more likely than downstream.

Two discernible ions in a trap represent a microscopic model system for the study of reaction kinetics.

Keywords: trapped ions, laser cooling, ion kinetics

1. Introduction

The confinement of individual ions in dc or ac electric and magnetic fields forming 'ion traps' [1] has numerous motivations most of which share the need of individually addressing the ions:

- The study of laser cooling by monitoring the kinetics of ion vibration in the trap [2].
- Quantum information processing, that requires individual ion preparation and read-out by radiation [3, 4].
- All measurements whose results are intended to consist of *eigenvalues*, as opposed to expectation values, that allow one to derive conclusions not accessible from averages [5, 6].
- Also, *ionic reactions* may take place, in a trap, and may be observed as individual processes.

Atomic and molecular collisions as well as reactions have been studied in the intersection region of atomic beams, where the control of the collisional kinematics is superior, whereas the identification of energy and internal states requires extensive filtering of the input and output beams [7]. In an ion trap, on the other hand, these latter parameters are well characterized, and in typical situations the individual collisional or reactive processes may be repeated over and over again, in real time.

The temporal variation of the molecular state during a reaction is conventionally plotted along a 'reaction coordinate', that is, as a function of a particular time-dependent variable. In simple diatomic reactions, this variable may be identified with the spatial relative coordinate of the two particles. Along this coordinate, characteristic quantities of the system may be plotted that vary in the course of the reaction. The most important quantity, the energy of the system, forms a bistable potential well whose minimum positions mark input and output states of the reactive system. Then, an exothermic or endothermic reaction corresponds, respectively, to the transition of the system from the initial metastable to the final stable state via the intermediate potential barrier, and vice versa.

We report an experiment on two equal ions confined in the potential well of an electrodynamic trap and made discernible,

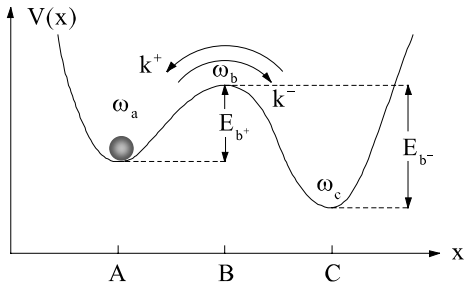

Figure 1. A particle in a bistable (A, C) potential well along a reaction coordinate x models a diatomic reaction. Here, $x_C = r_0$ and $x_A = -r_0$ are the steady-state distances of two trapped *and localized* ions. The transition A–C models the exchange of ion positions when the ions overcome the barrier E_b by thermal excitation.

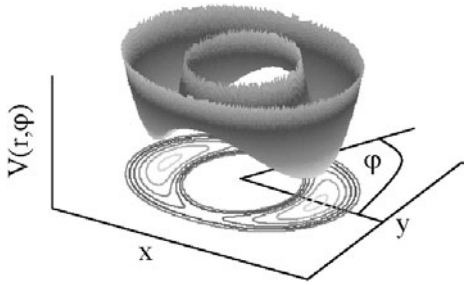

Figure 2. The distribution of the effective potential of two ions in the $z = 0$ plane of the trap: the superposition of the trapping potential and Coulomb repulsion results in an almost circular valley or 'moat'-shaped potential whose floor shows two wells in opposite positions ($\pm x_0$, $y = 0$), separated by two barriers.

that embodies the most fundamental picture of a diatomic reaction. The inverse reaction is also thermally excited, and the reiteration of the reaction and its inverse may be observed for arbitrarily long duration of time.

2. Ion kinetics in a bistable potential well

Figure 1 shows a bistable potential distribution versus the reaction coordinate x with the system initially in its metastable state. The thermally induced hopping via the potential barrier and decay into the stable state takes place at a rate that was found exponential more than a hundred years ago by Arrhenius [8]. Later, Kramer determined the coefficient to this exponential, and the rate constant of the reaction is

$$K_{A-C} = \frac{\omega_a}{2\pi}\rho\left(\frac{\gamma}{\omega_b}\right)\exp\left(-\frac{E_b}{k_B T}\right), \tag{1}$$

where ω_i is a local oscillation frequency derived from the curvature of the potential at location i, ρ is a function of the ratio of the heating (or cooling) rate γ and of ω_b, and E_b is the activation energy [9]. The equation of motion of the two-particle system in the potential is

$$M\ddot{x} = -\frac{\partial V}{\partial x} - \gamma M\dot{x} + \xi(t), \tag{2}$$

where M is the reduced mass of the system, $V(x)$ is the bistable potential, and ξ is a thermal Langevin force modelling fluctuations, from the light interaction, where $\xi(t)\xi(t') = \delta(t - t')$ [10]. Such a potential has been represented recently by the radiative dipole force, or 'gradient' force, acting on classical microscopic particles in two overlapping light beams, and the kinetics of the particles in this double potential well has been investigated [11].

3. Two ions in an electrodynamic trap

In the present experiment, two $^{138}Ba^+$ ions have been confined in the pseudopotential of a miniaturized electrodynamic trap. This harmonic pseudopotential results from the ponderomotive force of an ac field generated by a high-frequency voltage between ring and cap electrodes. The potential for the *relative* motion of the two ions is modified by Coulomb repulsion ($r^2 = x^2 + y^2 + z^2$):

$$V(r) = \frac{M}{4}(\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) + \frac{e^2}{4\pi\epsilon_0 r}. \tag{3}$$

A slight deviation of the trap's ring electrode from toroidal symmetry leaves the slope of the pseudopotential in one radial direction (say, y) steeper than in the orthogonal one (x). Along the trap axis (z), the slope is actually steepest. Consequently, the corresponding vibrations of a single ion in three spatial directions somewhat differ in frequency, as $\omega_z > \omega_y > \omega_x$. The combined potential well for two ions forms a spheroidal shell with minimum positions at $r_0 = (x_0, y_0, z_0) = (\pm 3, 7\ \mu\text{m}, 0, 0)$. For a visualization, we restrict the discussion to the central plane of the ring electrode ($z = 0$). This restriction is sufficient even for quantitative modelling of the ion kinetics, when the vibrational excitation of the ions is low enough not to make them leave this plane. Here, the combined potential forms a 'moat' whose floor is shaped as two opposite troughs, at the minimum positions (figure 2). The local vibrational frequencies in these troughs are

$$\tilde{\omega}_x = \sqrt{3}\,\omega_x, \qquad \tilde{\omega}_{y,z} = \sqrt{\omega_{yz}^2 - \omega_x^2}, \tag{4}$$

such that, with a typical realization,

$$(\tilde{\omega}_x, \tilde{\omega}_y, \tilde{\omega}_z) = (1.738, 0.183, 0.319) \times 2\pi\ \text{MHz}. \tag{5}$$

The two wells, at the minimum positions, are separated, in the azimuthal direction, by two barriers whose height,

$$\Delta\tilde{V} \propto \omega_y^{2/3} - \omega_x^{2/3}, \tag{6}$$

is actually 6.4 μeV, in this realization. These barriers, at finite y and $x = 0$, prevent the ions from assuming an azimuthally delocalized state and forming a ring-shaped 'plasma'. Thermally excited motion is restricted to the ring-shaped floor of the potential well, and the equation of 1D motion is reduced to

$$Mr\ddot{\varphi} = -\frac{1}{r}\frac{\partial\tilde{V}}{\partial\varphi} - \gamma Mr\dot{\varphi} + \xi(t), \tag{7}$$

with

$$\tilde{V}(r, \varphi) = r^2(k_x \cos^2\varphi + k_y \sin^2\varphi) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{2r}, \tag{8}$$

where k_i is the force constant in direction i (figure 3).

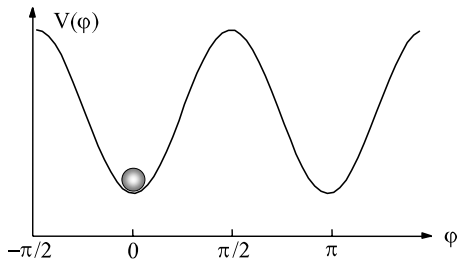

Figure 3. The bistable potential well along the azimuthal coordinate φ of two trapped ions.

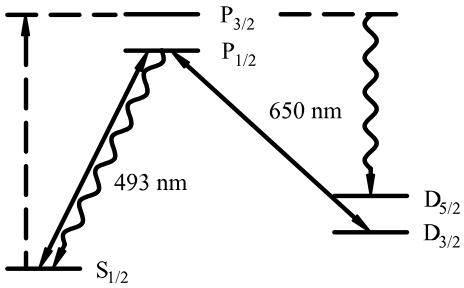

Figure 4. The lowest energy levels of Ba^+, and laser excitation.

4. The experiment

The relevant energy levels of $^{138}Ba^+$ are shown in figure 4. On the resonance line $S_{1/2}$–$P_{1/2}$, resonant scattering from the ions is excited by 493 nm light from a tunable, narrow-band, and frequency-doubled diode laser. In order to prevent optical pumping into the low-lying metastable level $D_{3/2}$, irradiation of the ions by repumping light from a tunable diode laser, or from a DMS dye laser, at 650 nm is required. Optional resonance light from a barium hollow-cathode lamp allows one to excite the ions on their $S_{1/2}$–$P_{3/2}$ resonance line and to optically pump them into their metastable $D_{5/2}$ state. Having been excited into that 'dark' state, a barium ion is kept from scattering blue resonance light.

The ionic sample (one or two ions) was confined in a 1 mm electrodynamic ('Paul') trap and irradiated by the coaxial and focused beams of the two lasers (figure 5). The flux of the resonantly scattered light was recorded by a photomultiplier in the photon counting mode. Simultaneously, in a second channel of observation, the ions were imaged by a spatially resolving photomultiplier, or alternatively by an intensified CCD camera. The signals from both channels have been subjected to data processing.

The strategy of observation included data acquisitions of the following kinds:

- Recording the integrated flux of resonance scattering of the Ba ions, versus stepwise scanning the red laser across the corresponding resonance. The resulting 'excitation spectra' have been made to fit in with calculated spectra, and the ion temperature has been determined from these fits.
- The images of the ions have been recorded at various steps of red-laser detuning. They have been found to represent either two separate, localized sources of fluorescence ('ion crystal'), or a ring-shaped structure ('plasma cloud'). These types of image have been correlated with the temperature values derived from the excitation spectra.
- With two localized ions, and with incoherent excitation to the $D_{5/2}$ 'dark' state by the lamp, the scattering of resonance light has been measured in time bins of 0.1 s duration, and time series of these measurements have been recorded. Three levels of light flux have been observed: light from both ions (2), light from one ion, the other one off (1), and no light, both off (0). In order to lift the degeneracy of signal 1 (that is, to distinguish the 'left' or 'right' ion found on), the fluorescence from one of the ions' sites was made imperfectly focused onto the photocathode of the PM, such that in fact *four* distinguishable levels of light flux appeared in the recorded signal, and the spatially localized ions were left discernible. When the desired signal (1) was recorded, the light from the lamp was blocked in order not to switch to signal level 0 or 2.

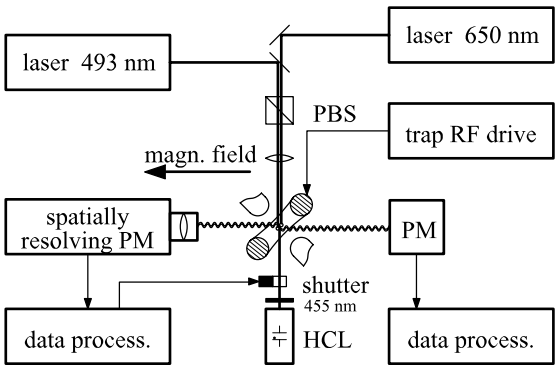

Figure 5. The experiment.

5. Laser heating and cooling the ions

The recorded excitation spectra show, in the low-frequency wing of the red-laser excited $D_{3/2}$–$P_{1/2}$ resonance, four zeros of fluorescence, which are well reproduced by calculations based on eight-level Bloch equations [12]. These particular frequency values represent 'dark' resonances [13] corresponding to four allowed combinations of two Zeeman sublevels in the $S_{1/2}$ ground state, and four sublevels in the $D_{3/2}$ metastable state. Whereas the contribution of the red laser to conventional Doppler cooling of the ions varies slowly and monotonically across this spectral region of red-laser detuning, the Raman contribution [14, 15] varies sensitively and makes, in the total rate of energy transfer, laser cooling alternate with laser heating of the ions (figure 6, bottom). The corresponding mean vibrational energy (or 'temperature') of the ions varies dramatically and shows four spectrally separated regions of high vibrational excitation (figure 6, centre). These regions are found to correspond to those images that show the regime of the ions forming a ring-shaped cloud. Obviously, the vibrational excitation by Raman heating makes the ions overcome the azimuthal barriers in their moat-shaped potential well and exchange their sites. On the other hand, the excitation seems not high enough to make the ions pass the much higher barrier that keeps them from moving, along the polar coordinate, in

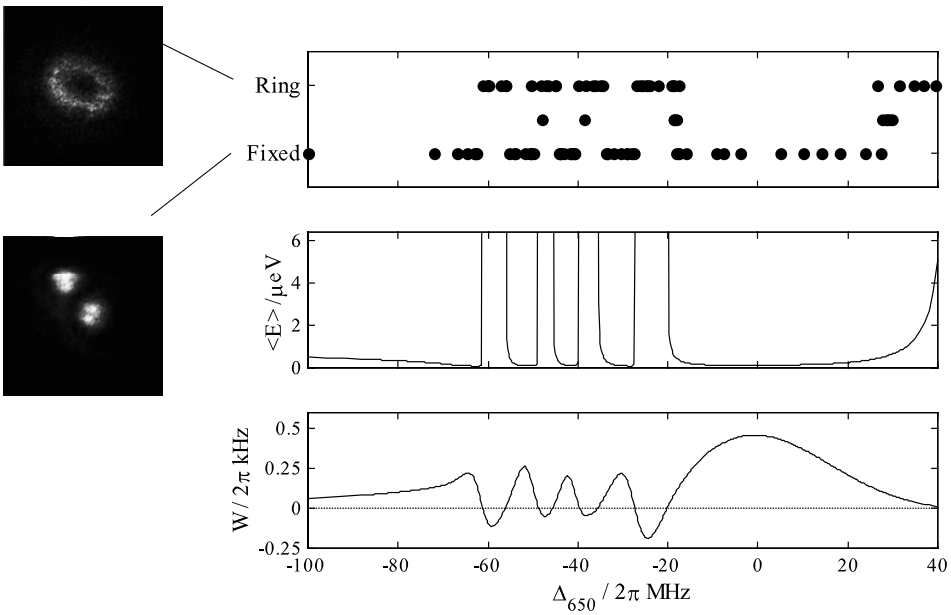

Figure 6. Types of ion image found in observations at varied detuning of red light: ions in separate fixed positions, a ring-shaped cloud, or an indefinite image (top). The net laser heating or cooling including the contribution of electronic Raman processes (bottom). The resulting steady-state kinetic energy, or temperature, of ions (centre). From [12].

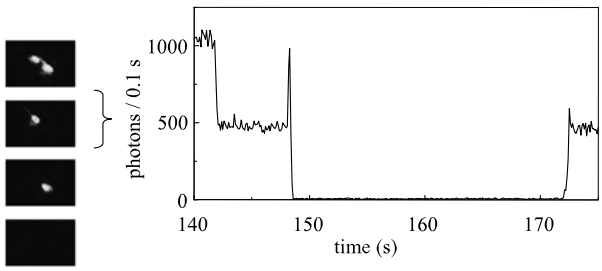

Figure 7. An example of a time series of the numbers resulting from photon counting during 0.1 s intervals (right). Corresponding images (left) of a sudden jump from signal level 1 to 2 prove the dark ion to be cold from sympathetic cooling by its bright companion. In contrast, *two dark* ions suffer spurious heating, and their orbits blow up with time. It needs about 1 s to re-cool them after one ion had become bright.

the axial direction, and forming a plasma ball. These findings confirm the assumption of thermally driven ion kinetics.

From time series of photon counting data, further details on heating and cooling of the pair of ions may be derived. Figure 7 shows such a time series, beginning with a short sequence of signals from both ions, followed by a longer sequence of one-ion signals, and a single data point with the signal from both ions. This result is followed by a 25 s period of no signal, and finally by a sequence of one-ion signals. The latter shows a 1 s onset, since laser cooling was missing during the preceding dark time. Spurious heating has blown up the ion cloud to macroscopic size corresponding to a negligible signal when light scattering happens again, and cooling down to the 'crystallized' state requires some time. From this result one estimates the rate of spurious heating, mainly by field fluctuations and parametric effects of the ac driving voltage, of the order of 50 ± 20 vibrational quanta per second. On the other hand, the jump from fluorescence level 1 to 2 demonstrates the ion pair to be well cooled: sympathetic cooling by the bright ion has been sufficient to prevent the dark one from becoming overly hot.

6. Thermally activated exchange of ion positions

Numerous time series of photon counting rates have been recorded, when one of the positions of a 'bright' ion had been discriminated from the other one, as outlined in section 4. An example of ten seconds' duration is shown in figure 8. From these time series, 'waiting times' of the system in the particular two states 'left' ion on, 'right' one off, and vice versa, have been extracted and subjected to statistical evaluation. The distributions of these waiting times show an exponential shape in agreement with the presumed thermally driven kinetics of the ions. The distributions (figure 8, right) are labelled by a temperature value, determined separately from the corresponding excitation spectra. Thus, each distribution is characterized by a mean waiting time, whose inverse is a measure of the probability of the ions exchanging their positions, i.e., of their 'jump rate'. The rates from all the distributions have been plotted as a function of the inverse vibrational ion temperature. It has turned out that the rates of the bright ion jumping *upstream* and *downstream* in the direction of light propagation systematically deviate from each other. The scattering force of the light seems to introduce a 20% asymmetry for the heights of the effective potential barriers seen by the bright ion when jumping in the two reciprocal directions (figure 9). The jump rate per 10^3 s is shown, versus $\Delta V/kT$, in figure 10, separately for both directions of the bright ion's jumping. The data confirm that the rates turn high at increasing ion temperature as required by thermal kinetics, although the growth, versus T, is surprisingly sudden. In contrast with expectation, the rate for upstream jumps exceeds the rate of downstream jumps. An estimation

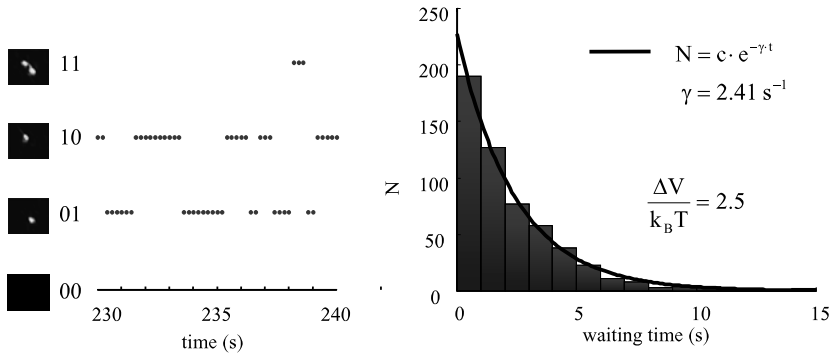

Figure 8. Time series of the numbers resulting from photon counting during 0.1 s intervals, when the signals of the ions in their two positions have been intentionally distinguished by recording one of them out of focus (left). Distributions of 'waiting times' show thermal distributions (right).

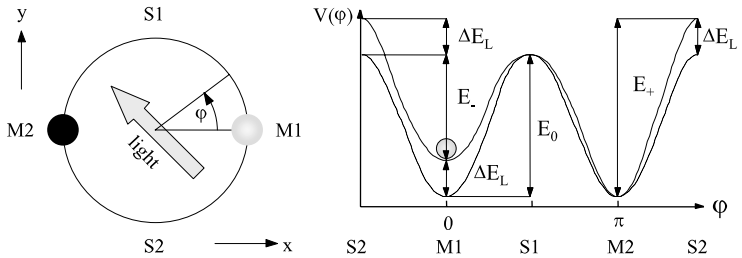

Figure 9. Positions of ions in the x–y plane of the trap, and the direction of light propagation (left). Bistable potential versus azimuthal angle φ, modified by the scattering light force. The effective increment ΔE_{L} of a potential supposed to be in upstream position M1 (right).

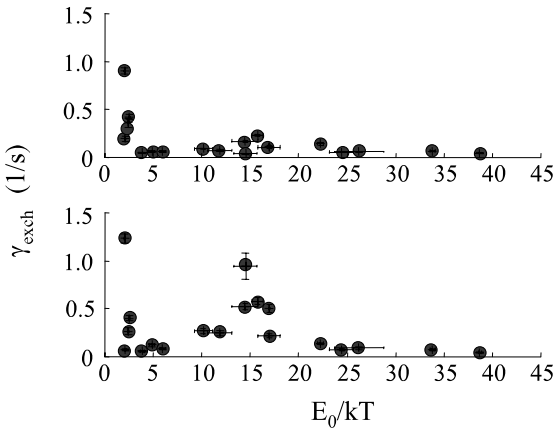

Figure 10. Rate of position exchanging jumps of the bright ion in the downstream direction (top) and in the upstream direction (bottom) versus normalized inverse temperature ($E_0/k_{\mathrm{B}}T$, where E_0 is the effective potential barrier). Note the resonant feature at $E_0/k_{\mathrm{B}}T \cong 15$.

shows that the dipole light force from the gradient of the light field outside the axis of the laser beam may in fact overcompensate for the effect of the light scattering force. The most conspicuous feature is the appearance of a resonance-like peak of the jump rate at $\Delta V/kT \cong 15$. Attempts at attributing this peak to stochastic resonance of the ions under periodic perturbation have failed so far. The decrease of the observed jump rate with growing T, on the high-temperature wing of the peak, may indicate, however, a strongly increased chance of *inverse* jumps correlated with primary jumps as a consequence of the ion pair's inertia in its rotational motion around the trap axis. Such an effect must tend to diminish the effectively recorded rate of the ions exchanging their sites.

7. Conclusions

A pair of ions have been stored in an electrodynamic trap, and their laser-excited resonance fluorescence has been detected by (i) photon counting of the light flux, and (ii) imaging the ions. Upon stepwise scanning the 650 nm laser light used for re-exciting the ions from the metastable $D_{3/2}$ level, the light force imposed upon the ions by electronic Raman interaction, and also the ions' net vibrational energy vary drastically. When well cooled, the ions are found separately localized. At reduced cooling rate, the ions, so far confined within their ring-shaped potential moat to their local wells, get thermally excited and overcome the two barriers on the floor of the moat. Now they are free to move in the azimuthal direction and form a ring-shaped plasma. The regimes of localized and delocalized ions coincide with the regimes of Raman cooling and heating, respectively.

Upon irradiation by incoherent resonant light at their $S_{1/2}$–$P_{3/2}$ resonance line, the ions may become pumped to the metastable $D_{5/2}$ state and cease to scatter resonance light. The two ion positions have been discriminated from each other by their different imagings on the photocathode of the photomultiplier. Thus, four levels of light flux of the ions' resonance radiation have been observed. Particularly informative are the two levels of light flux, where one ion is dark, the other one bright. Time series of photon numbers resulting from counting over fixed time intervals have been recorded, and the distributions of waiting times have been derived. The corresponding mean rates of 'jumps', i.e. of the two ions exchanging their positions, vary with ion temperature: a high jumping rate correlates with high temperature, although the expected gradual increase is not observed. The rates of the bright ion jumping *upstream* in the light exceed the rates in the

other direction, probably as an effect of the dipole light force exceeding the scattering force. The observed peaking of the jump rate at a temperature corresponding to about 7% of the energy barrier is attributed to the strongly enhanced chance of correlated back-jumping upon increasing temperature.

The observed interchange of fluorescence emission between the ions' sites might be thought to be caused by a different process, namely by the exchange of ion *excitation*, as opposed to exchanging positions. We have observed time series for photon counting the scattered light with pairs of isotopically different ions also: here, one of the ions was found permanently dark, or very weakly excited only, as a consequence of its isotope shift. The observed rates of switching of the fluorescence between the two ion sites have been found compatible with those observed with equal ions one of which was dark *temporarily* when excited to its $D_{5/2}$ metastable state. These findings seem to verify the assumption of ion jumps exchanging their positions.

The reported experiments show that two ions confined in an ion trap may serve as a useful microscopic model of diatomic reaction kinetics.

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