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# Blackbody thermometry with cold molecular ions and application to ion-based frequency standards

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We have used laser spectroscopy to measure the rotational level distribution of trapped molecular HD$^+$ ions at translational temperatures in the millikelvin range. The HD$^+$ ions are loaded into an ion trap by electron-impact ionization, and sympathetically cooled using laser-cooled Be$^+$ ions which are already stored in the trap. Under our experimental conditions, the internal (rotational) degrees of freedom turn out to be independent of the translational degrees of freedom, and an effective rotational temperature close to room temperature is found. The near absence of background-gas collisions allows the rotational temperature to be related directly to the temperature of the ambient blackbody radiation (BBR). This feature suggests the use of molecular ions for BBR thermometry, which may help to improve the accuracy of frequency standards based on trapped atomic ions. For the spectroscopic measurement of the rotational populations, we propose a nondestructive technique.

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## I. INTRODUCTION

Blackbody radiation (BBR) is ubiquitous in the physical world. In particular, for spectroscopy of atoms and molecules, the presence of BBR has a significant influence on measurement and analysis. For polar molecules, room-temperature BBR can have a strong influence on the population distribution of rotational and vibrational states if collisions are infrequent. This can affect the shape and resolution of molecular spectra to a large extent. BBR also has a detrimental effect on the storage time of neutral polar molecules in an electrostatic trap [1]. For atoms, BBR-induced shifts to transition frequencies are often very small; however, they contribute significantly to the inaccuracy of atomic frequency standards [2–4].

Measurement of the rotational distribution of an ensemble of molecules is a common method to obtain information on the internal temperature. The internal (rovibrational) degrees of freedom of diatomic, polar molecules couple strongly to the electric component of the BBR field. In the absence of inelastic collisions with background-gas constituents, the internal temperature of a polar molecule is determined completely by BBR, and polar molecules thus might be used to probe the BBR field. Such conditions may be achieved with cold molecular ions stored under ultrahigh-vacuum conditions. For typical ion traps, trapping frequencies are of order 1 MHz or less, whereas rotational and vibrational frequencies are much larger than 1 GHz. Therefore, no strong couplings of the translational degrees of freedom to the internal degrees of freedom are expected to exist, as indicated by the experimental work of Bertelsen *et al.* [5]. Thus, for an isolated polar molecular ion, any method to measure the populations of those internal states which interact with BBR might be used to find the temperature of the BBR field.

In this paper, we demonstrate how trapped molecular ions can be used as a probe of the BBR field. We will first describe an experiment in which we determined the BBR temperature via spectroscopy of HD$^+$ molecules (Sec. II). Having established the possibility of using cold, trapped molecular ions as BBR thermometers, we propose the use of molecular ions for BBR thermometry in ion traps for optical clocks in Sec. III. A nondestructive method for detecting rotational state populations is proposed in Sec. III A. The effect of BBR on the frequency measurement of atomic clock transitions is discussed briefly in Sec. III B, as well as several candidate molecular ions for BBR thermometry. The results of this work are summarized in Sec. IV.

## II. EXPERIMENTAL DETERMINATION OF THE BLACKBODY TEMPERATURE USING HD$^+$

### A. Theoretical background

At room temperature, the nuclear vibration of HD$^+$ (vibrational constant $\omega_e \approx 2000\ \text{cm}^{-1}$) is virtually frozen out, i.e., each HD$^+$ ion is in its vibrational ground state. On account of its small reduced nuclear mass, HD$^+$ has a relatively large rotational constant, $B_0 \approx 22\ \text{cm}^{-1}$. Consequently, only the seven first rotational levels are significantly populated at room temperature, where the fractional populations $f_{v,J}(T)$ are given by

$$f_{v,J}(T) = f_{0,0}(T)(2J+1)e^{-E_{v,J}/k_B T}. \tag{1}$$

The rovibrational energies $E_{v,J}$ have been calculated to high accuracy for HD$^+$ [6,7]. For the present analysis, however, it is sufficient to use the energies obtained by solving the radial Schrödinger equation for the *ab initio* potential energy curve given by Esry and Sadeghpour [8]. This also produced rovibrational wave functions, which were subsequently used to find the expectation values $\mu_{v'J',vJ}$ of the dipole moment function, also given in Ref. [8]. Good agreement with previous values for $\mu_{v'J',vJ}$ is found [9]. The interaction of BBR with the rotational degrees of freedom is described by the Einstein rate equations, where the Einstein coefficients are given by

$$A_{v'J',v''J''} = \frac{\omega^3}{3\pi\epsilon_0\hbar c^3}\frac{S_{J',J''}}{2J'+1}\mu^2_{v'J',v''J''}, \tag{2a}$$

$$B_{v'J',v''J''} = \frac{\pi^2 c^3}{\hbar\omega^3}A_{v'J',v''J''}, \tag{2b}$$

$$B_{v''J'',v'J'} = \frac{2J'+1}{2J''+1} B_{v'J',v''J''}. \tag{2c}$$

Here, the primed (double-primed) quantities refer to the upper (lower) state of the transition, and $\omega$ is the angular frequency of the transition. $S_{J',J''}$ is given by the Hönl-London formulas [10]. The BBR spectral density, for a given temperature $T$, used in the rate equations is

$$\rho_T(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_B T} - 1)}. \tag{3}$$

The rate equations can be modified to include the interaction with laser radiation inducing rovibrational transitions in $HD^+$, as is the case in our experiment.

### B. Experimental setup

#### *1. Trapping, sympathetic cooling and detection of HD$^+$*

Details of the setup and the method to obtain trapped, sympathetically cooled $HD^+$ ions were already described in Refs. [11,12]. In brief, we trap ~2000 $Be^+$ ions in a linear radio-frequency trap, and they are brought to temperatures of ~10 mK by means of (Doppler) laser cooling at 313 nm. We monitor the fluorescence level at 313 nm with a photomultiplier tube. At these temperatures, the beryllium ions arrange themselves in an ordered state referred to as a Coulomb crystal. $HD^+$ ions are loaded into the trap by electron-impact ionization of neutral HD gas, after which they are sympathetically cooled to ~20 mK by the $Be^+$ ions and become embedded inside the Coulomb crystal. The presence of $HD^+$ manifests itself as a change in the 313 nm $Be^+$ fluorescence when the $HD^+$ radial (secular) motion in the ion trap is resonantly driven by an ac electric field. For typical intensities and detunings below resonance of the 313 nm laser, the fluorescence rises if the $HD^+$ motion is excited. The rise in fluorescence is approximately linearly proportional to the number of trapped $HD^+$ ions, and can be explained as follows. Driving the $HD^+$ motion sympathetically heats the $Be^+$ ion crystal, and the resulting elevated temperature of the $Be^+$ ions leads to a stronger cooling action by the 313 nm laser, i.e., more photons from the cooling laser are scattered by the $Be^+$ ions.

#### *2. Rovibrational spectroscopy of HD$^+$*

Recently, we have demonstrated rovibrational spectroscopy of $HD^+$ through $(1+1')$ resonance-enhanced multiphoton disscociation (REMPD) [12]. The REMPD process is depicted schematically in Fig. 1. The first photon (with wavelength 1.4 $\mu$m) drives a $(v'=4,J') \leftarrow (v''=0,J'')$ overtone transition within the electronic ground state of $HD^+$. Population in the $v=4$ state is consecutively dissociated by the second photon at 266 nm. This leads to loss of $HD^+$ ions from the trap, which is monitored with the secular excitation method described above. In our previous work we used this method, aiming at high resolution of the $(v'=4,J') \leftarrow (v''=0,J'')$ spectra, which show hyperfine structure spanning roughly 180 MHz about the deperturbed transition frequency. Here, we will be merely interested in driving "pure" rovibrational transitions in order to infer the rotational populations $f_{0,J}(T)$ in the vibrational ground state. To this end, we dither our laser, thereby broadening it to 200 MHz (full width at half maximum). Tuning the laser to the deperturbed frequency then ensures that all hyperfine components are simultaneously addressed.

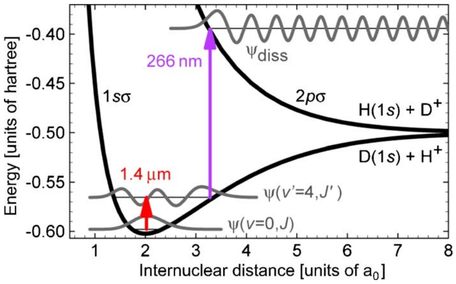

FIG. 1. (Color online) Principle of $(1+1')$ REMPD spectroscopy of $HD^+$ ions. A tunable infrared diode laser excites a rovibrational overtone transition $(v'=4,J') \leftarrow (v''=0,J'')$. The $HD^+$ ions excited to the $v=4$ vibrational level are dissociated using 266 nm laser radiation: $HD^+$ $(v'=4) + h\nu_{266\text{ nm}} = H + D^+$ or $H^+ + D$. Due to different Franck-Condon wave function overlaps, the calculated uv absorption cross section from the $(v=4)$ level $(\sim 2.4 \times 10^{-17}\text{ cm}^2)$ is about seven orders of magnitude larger than that from $v=0$ [13,14]. Energy values represent total binding energies of the molecule.

### C. Method and results

Our experiment aims at the determination of the rotational temperature $T$ from experimentally determined populations $f_{0,J}(T)$. This is accomplished as follows. We tune the 1.4 $\mu$m laser to a specific transition $(v'=4,J+1) \leftarrow (v''=0,J)$ within the $R$ branch, where $J=0,1,\ldots,7$. The laser is calibrated versus a GPS-referenced frequency comb with submegahertz accuracy [15], whereas the frequency drift of the laser during the course of the experiment is smaller than 15 MHz. The transition frequencies used here are the *ab initio* results given by Balint-Kurti *et al.* [6]. The expected accuracy of these results is 6 MHz, which is in good correspondence with a recent precision measurement of the $(v'=4,J'=3) \leftarrow (v''=0,J''=2)$ transition [15]. Next, we execute a cycle consisting of quasicontinuous secular excitation (QSE) of the $HD^+$ trap motion for a 5 s time interval, followed by a 0.4 s period of REMPD, and ending with another 5 s of QSE (see Fig. 2). For an optimum signal-to-noise (SN) ratio, we use the 1.4 $\mu$m laser at its maximum power (1.3 mW). The duration of the REMPD pulse is kept as short as possible to minimize the effect of repopulation of the lower level via BBR, which sets in on a time scale of seconds, without compromising the SN ratio. We record the 313 nm fluorescence and fit linear segments to the fluorescence levels during the QSE. The slope of each segment takes into account slow drifts of the fluorescence level, which are caused by the loss of $HD^+$ in collisions with background gas, and by slow variations in the laser power and frequency. The discontinuity between the two segments at time $t_h$, at the end of the REMPD pulse, gives the fractional loss of $HD^+$ due to the REMPD process only (Fig. 2). To

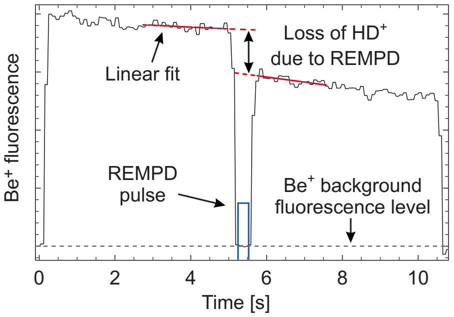

FIG. 2. (Color online) Experimental cycle of REMPD and detection of loss of $HD^+$ using the method of quasicontinuous secular excitation. During the REMPD pulse the QSE is off, and the fluorescence drops to the background level. Linear segments are fitted to the fluorescence during secular excitation, the slopes of which are determined by all loss processes other than the REMPD. The discontinuity between the extrapolated fitted segments thus gives a measure for the loss of $HD^+$ due to the REMPD process only.

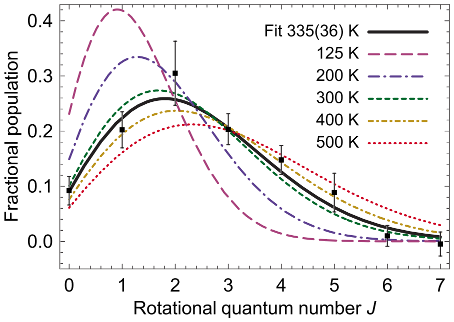

FIG. 3. (Color online) Dashed curves are $HD^+$ rotational distributions (in the vibrational ground state $v=0$) at various temperatures, as given by Eq.(1). The data points are the average rotational populations inferred using REMPD spectroscopy of $(v'=4,J+1) \leftarrow (v''=0,J)$ transitions in $HD^+$. The black curve represents an unweighted fit of the rotational distribution to the data, resulting in $T=335(36)$ K.

reduce the effect of possible slow drifts occurring on the time scale of the entire experiment (2.5 h), we apply only ten consecutive cycles per transition before moving on to another transition. Once all eight transitions have been addressed, the procedure is repeated until each transition has been subject to 30 cycles. During the procedure, some of the $Be^+$ ions are lost from the trap, mostly through chemical reactions with neutral HD gas during the loading of $HD^+$ ($HD^+$ needs to be reloaded every 3–9 cycles). To compensate the gradual loss of $Be^+$, we load extra $Be^+$ into the trap every ~100 cycles.

Now, let $p_J(T)$ be the measured fractional loss of $HD^+$, sustained during a single cycle due to the REMPD process only, where $T$ is the rotational temperature of the molecules. The fractional populations $f_{0,J}(T)$ are related to the $p_J(T)$ in a nontrivial way, since the REMPD process (which depletes the lower rotational level $J$) competes with the repopulation of level $J$ mediated by BBR and which involves all populations within the rotational manifold. To infer $f_{0,J}(T)$ from the measured $p_J(T)$, we simulate the experimental cycle using the Einstein rate equations and obtain a theoretical value for the ratio $\tilde{f}_{0,J}(T)/\tilde{p}_J(T)$ (the tilde indicates results from the simulation). This value depends only weakly on the laser intensities used, and the uncertainty in the measured intensities has a marginal effect on the final measurement uncertainty. However, this approach forces us to assume a certain value $T_0$ for the BBR temperature, which affects the simulation through $\rho_T$ and the initial state populations given by Eq. (1). As an initial guess, we assume $T_0=300$ K to find $\tilde{f}_{0,J}(T_0)/\tilde{p}_J(T_0)$. For each $J$, we multiply this ratio by the measured value $p_J(T)$ to find intermediate values $f_{0,J}(T_1)$, where $T_1$ is found by fitting the distribution in Eq. (1) to the intermediate values $f_{0,J}(T_1)$. We subsequently run the simulation again, this time with $T_1$ as input temperature, which gives improved ratios $\tilde{f}_{0,J}(T_1)/\tilde{p}_J(T_1)$. Multiplying again with $p_J(T)$ gives $f_{0,J}(T_2)$, where $T_2$ is again found by fitting the rotational distribution. It should be noted that this approach directly yields the fractional populations, i.e., no overall scaling factors are involved. Three consecutive iterations give a final rotational temperature of 335 K, with 1 K convergence. This is much smaller than the 36 K uncertainty in the fitted temperature, which stems primarily from random fluctuations in the decay values $p_J(T)$, and possible unidentified $J$-dependent systematic offsets. The final fitted rotational distribution function is plotted in Fig. 3, together with several distribution functions at other temperatures. Our result clearly indicates that sympathetic cooling of molecular ions to millikelvin temperatures in an ion trap has a negligible effect on the internal (rotational and vibrational) degrees of freedom. This contrasts with another cooling method for trapped molecular ions, collisions with a cryogenic buffer gas [16]. The independence of the translational and internal degrees of freedom observed in our experiment can be attributed to the fact that internal transitions have frequencies exceeding 1 THz, whereas typical trap frequencies are on the order of 1 MHz or less. As a consequence, couplings between the different degrees of freedom must be either highly nonresonant, or of very high order, and therefore weak. We note that hyperfine populations may be influenced by the trap motion in the presence of magnetic field gradients, as magnetic hyperfine transition frequencies and trap frequencies are of the same order of magnitude. However, such effects are eliminated by dithering our probe laser over the entire hyperfine spectrum.

The rotational temperature might be affected by inelastic collisions with background-gas constituents. Here we consider collisions with neutral $H_2$ only, which is likely the most abundant background-gas constituent. Internal-energy transfer will take place only during Langevin spiraling collisions, when the collision partners form a transient molecular complex. Therefore, we can put an upper limit on the collision rate using the rate of Langevin collisions of a charged ion with $H_2$ [17],

$$\gamma_c = \frac{qP}{k_B T}\sqrt{\frac{\pi\alpha}{\epsilon_0\mu}}. \tag{4}$$

Here, $q$ is the charge of the ion, $\mu$ represents the reduced mass of the $HD^+$-$H_2$ collisional system, and $\alpha$ stands for the polarizability volume of $H_2$. $P$ is the $H_2$ partial pressure, which is smaller than $10^{-8}$ Pa in our apparatus. From Eq. (4), we find an upper limit on the inelastic collision rate at $T=300$ K of $0.005\ \mathrm{s}^{-1}$. For comparison, the total BBR-induced transition rate (at 300 K) is larger than $0.44\ \mathrm{s}^{-1}$ for rotational levels $J>0$, and equals $0.11\ \mathrm{s}^{-1}$ for $J=0$. Thus, we can safely ignore the effect of collisional relaxation, and we interpret the rotational temperature found as the BBR temperature.

## III. NONDESTRUCTIVE SPECTROSCOPY AND BBR THERMOMETRY WITH MOLECULAR IONS

### A. Nondestructive and state-selective detection of molecular ions

The experiment described in Sec. II shows that trapped molecular ions can be used to determine the temperature of the BBR field. The ~30 K inaccuracy of the temperature measurement could, in principle, be improved by including more data points. Since the procedure for reloading $HD^+$ ions into the trap takes much longer (~60 s) than the ~15 s for rethermalization by the BBR, an additional speedup in the data-taking rate would result if the spectroscopy were done nondestructively. Such a scheme would also remove the need for a suitable transition for dissociation of the molecule. Furthermore, it would be more suitable for spectroscopy and manipulation of single molecular ions: high-resolution spectroscopy and quantum information processing with single atomic ions typically rely on nondestructive detection [18]. Previously, the rotational state of a single $CO^+$ ion in a cryogenically cooled Penning trap has been measured nondestructively by detection of a polarization-induced shift to the cyclotron frequency [19]. Here, we propose a nondestructive scheme for molecular spectroscopy, which may be readily implemented in a typical optical clock apparatus. With the application of BBR thermometry in ion-based optical clocks (Sec. III B) in mind, we propose to use an ion crystal containing one or several molecular ions, and one typical clock ion. The molecular ions could be used for BBR thermometry. For simplicity, we assume a linear ion crystal consisting of one typical clock ion, and one molecular ion. This does not preclude the application of this method to larger ion ensembles, as we will show below. The harmonically bound ions resemble a system of oscillators which are coupled through their mutual Coulomb repulsion [20], and the ion crystal thus possesses a corresponding set of normal modes. The clock ion is assumed to have a strong cycling transition which allows laser cooling of all modes of the ion crystal, whereas the narrow clock transition permits resolved observation of sideband transitions on any of the modes. These features allow the determination of the mean number of motional quanta in a specific normal mode after laser cooling to ~1 mK temperature [21]. The spectroscopy can now be realized by introducing a mechanism which significantly heats a particular normal mode (here designated as the "bus" mode), but which is present only when the molecular ion is in a specific rotational state. To realize such a mechanism, we propose to use an optical dipole force, modulated at the frequency of the bus mode. Previously, this technique was used to realize a geometric phase gate for trapped atomic ion qubits [17,22]. State-selective detection is accomplished by tuning the wavelength of the optical dipole laser near a transition starting from the rotational level of interest, meanwhile maintaining a considerably larger detuning from transitions that connect other rotational levels. As will be shown below, near unit detection efficiency of a single rotational state might be achieved, depending on the strength of the dipole force heating mechanism compared to other heating mechanisms occurring in the trap. Then, for each level of a given set of rotational levels, measurement of the bus-mode heating rate would allow the determination of its time-averaged population. The populations, in turn, reveal the rotational temperature of the molecule.

It should be noted that the methods described here assume an ideal BBR spectrum with a single temperature. As further explained in Sec. III B, the actual BBR spectrum inside an apparatus may deviate from this ideal spectrum. The method proposed here does not reveal such a deviation; however, by using different (isotopomers of) molecules, different parts of the BBR spectrum can be probed. The combined BBR information, obtained from these molecules with the proposed method, could enable a reconstruction of the shape of the BBR spectrum.

As a concrete example of the nondestructive method proposed above, we consider $CO^+$ as the thermometry ion. The modulated optical dipole force (MODF) is realized using the $(v'=3\leftarrow v''=0)$ band of the $A\ {}^2\Pi \leftarrow X\ {}^2\Sigma^+$ electronic transition. This electronic transition has been subject to many studies in relation with its appearance in the emission spectrum of comet tails. The $(v'=3\leftarrow v''=0)$ band origin corresponds to a wavelength of 401 nm, and experimental molecular constants are available allowing the prediction of level energies with ~ gigahertz accuracy [23]. The electronic part of the dipole transition matrix element has been calculated by Rosmus and Werner [24], and the Franck-Condon factor for the $(v'=3\leftarrow v''=0)$ band is 0.18 [23]. This leads to a transition dipole moment of about $0.1ea_0$. The lifetime of the $A\ {}^2\Pi$ upper state has been measured and calculated by several authors and amounts to ~3 $\mu$s (see [24] and references therein).

The MODF can be realized by overlapping two laser beams such that their respective wave vectors $k_i$ $(i=1,2)$ add up to an effective wave vector $\Delta k \geqslant k_i$ along the axis of the ion crystal. The frequency of both laser beams is detuned by ~1 GHz from a particular line $J'$-$J''$ in the $(v'=3\leftarrow v''=0)$ band, while the mutual detuning between the beams is near the frequency of the axial stretch mode (which acts as the bus mode here). For traps operating in the Lamb-Dicke regime for optical wavelengths, the mode frequencies are typically 1–10 MHz. This configuration of laser beams creates a running standing wave, which exerts a periodic force on the $CO^+$ ion only, provided it is in the particular level $(v''=0,J'')$. If the frequency of this force is tuned to the frequency of the stretch mode, it will resonantly excite its amplitude. We will assume that the stretch mode of the ion crystal has been cooled to the motional ground state using the narrow optical clock transition [25]. From the Schrödinger equation for this system (see, e.g., [17]), it can be shown that two beams with a power of 8 mW per beam, focused to an 80 $\mu$m waist at the position of the ions, can heat the stretch mode out of the ground state within 30 $\mu$s. This is much shorter than the lifetime due to off-resonant spontaneous emission from the $A\ ^2\Pi$ state, which we estimate to be ~50 ms for the 1 GHz detuning assumed above. The heating time is also much faster than the motional heating time caused by fluctuating stray electric fields at the location of the ion, which for most traps takes place on time scales longer than 1 ms [26]. It is noteworthy that such stray fields, caused by fluctuations of the potentials of the trap electrodes, are rather uniform on the length scale of the ion crystal; therefore, the stretch mode is relatively insensitive to this kind of trap heating as compared to the center-of-mass mode [27]. The heating event can be detected by probing the red sideband of the stretch mode on the clock transition: only if heating occurs will the red sideband become visible, and therefore near unit efficiency in the detection might be feasible.

Instead of detecting heating out of the motional ground state of a few-ion crystal, the MODF might also be used for state-selective detection of ions in a large crystal, similar to those described in Sec. II B 1. In this case, the MODF would simply replace the ac electric field for excitation of the secular motion (Sec. II B 1).

### B. Application of BBR thermometry to ion-based optical clocks

The presence of BBR in atomic frequency standards gives rise to a frequency shift of the clock transition which is known only to within a certain accuracy. For frequency standards based on a magnetic clock transition, the ac Zeeman shift caused by the BBR field adds to the uncertainty in the clock frequency. Besides the limited accuracy to which Zeeman Hamiltonians are known, the uncertainty stems from inadequate knowledge of the exact form of the BBR spectrum. For example, in cesium fountain frequency standards, the BBR shift gives rise to the largest systematic uncertainty in the clock accuracy ($\approx 3\times 10^{-16}$ relative uncertainty), which is almost entirely due to the uncertainty in the BBR temperature [28]. The exact form of the BBR spectrum depends on the temperature distribution of the structure surrounding the atomic ensemble being interrogated, as well as on its geometry and emissivity. (Spectral) emissivities are generally not accurately known, and the spatial temperature distribution can be nontrivial in systems in which local heating due to dissipation of electric currents occurs.

Also in optical atomic clocks BBR is a source of inaccuracy; in this case it causes a (quadratic) Stark shift to the optical clock transition. Again, the uncertainty has two origins: the differential electric polarizability $\sigma_S$ (which is known from atomic structure calculations [4] or measurement [29]), and the unknown exact shape of the BBR spectrum. Typical room temperature (relative) BBR shifts are of the order $10^{-15}$, causing $\sim 1\times 10^{-16}$ inaccuracy [30–35]. Two ion-based optical clocks have considerably smaller shifts: the liquid-helium-cooled $^{199}$Hg$^+$ clock, which has a shift that is reduced by $10^7$ from the room temperature value [29,36], and the $^{27}$Al$^+$ clock, having a relative shift of $8(3)\times 10^{-18}$ [29] due to nearly canceling polarizabilities of the upper and lower levels of the clock transition. In view of the search for a temporal variation of the fine structure constant $\alpha$, it will be desirable to compare a variety of atomic clocks based on different species [37]. Such a comparison might therefore benefit from reduction of the inaccuracy caused by BBR in all involved atomic clocks.

Although we anticipate that nondestructive spectroscopy of CO$^+$ is well feasible, it is likely not the best suited candidate for BBR thermometry. The main reason is that every measurement of the thermal rotational state causes a projection onto a nonthermal state, so that the next measurement cannot take place before the rotational state of the molecule has rethermalized. The rotational constant of CO$^+$, however, is relatively small compared to that of HD$^+$ and other diatomic hydride ions. This reduces the magnitude of the Einstein $B$ coefficients, and makes the rethermalization process rather slow (about 200 s at room temperature). Diatomic hydride ions, on the other hand, rethermalize about as fast as HD$^+$, and are more promising candidates for BBR thermometry. In laser-cooled ion experiments, hydrides of the laser-cooled species are a frequently encountered by-product: collisions of background-gas molecules (mostly neutral H$_2$) with laser-cooled ions in their excited state are often exothermic. Morse potential molecular constants for several common metal-hydride ions are available [38–40]; however, spectroscopic accuracy for the vibrational level energies has not yet been reported. Even so, BBR thermometry using ensembles of HD$^+$ as demonstrated above remains a possibility.

## IV. SUMMARY

We have measured the rotational temperature of trapped molecular ions at millikelvin temperatures. Our result shows that the coupling between internal degrees of freedom of the molecules to translational degrees of freedom is small compared to the coupling with blackbody radiation. The virtual absence of inelastic collisions allows direct relation of the rotational temperature to the temperature of the BBR radiation field. The use of trapped molecular ions for BBR thermometry may find application inside trapped-ion optical clocks, as part of the determination of the BBR frequency shift to the clock transition. This may be useful especially in rf traps, where dissipation of the ac trap-drive current can lead to significant local heating of the trap electrode surfaces, and estimating the *in situ* BBR temperature may be problematic. In addition to the demonstrated thermometry based on HD$^+$, we propose a spectroscopic method to infer the rotational distribution in diatomic molecules, which are trapped simultaneously with a typical clock ion. The method relies on state-dependent observation of heating of the molecular motion by a modulated optical dipole force, similar to that used for geometric phase gates performed on trapped ion qubits [22].

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[1] S. Hoekstra, J. J. Gilijamse, B. Sartakov, N. Vanhaecke, L. Scharfenberg, S. Y. T. van de Meerakker, and G. Meijer, Phys. Rev. Lett. **98**, 133001 (2007).

[2] W. M. Itano, L. L. Lewis, and D. J. Wineland, Phys. Rev. A **25**, 1233 (1982).

[3] W. M. Itano, J. Res. Natl. Inst. Stand. Technol. **105**, 829 (2000).

[4] E. J. Angstmann, V. A. Dzuba, and V. V. Flambaum, Phys. Rev. A **74**, 023405 (2006).

[5] A. Bertelsen, S. Jørgensen, and M. Drewsen, J. Phys. B **39**, L83 (2006).

[6] G. G. Balint-Kurti, R. E. Moss, I. A. Sadler, and M. Shapiro, Phys. Rev. A **41**, 4913 (1990).

[7] V. I. Korobov, Phys. Rev. A **74**, 052506 (2006).

[8] B. D. Esry and H. R. Sadeghpour, Phys. Rev. A **60**, 3604 (1999).

[9] E. A. Colbourn and P. R. Bunker, J. Mol. Spectrosc. **63**, 155 (1976).

[10] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).

[11] P. Blythe, B. Roth, U. Fröhlich, H. Wenz, and S. Schiller, Phys. Rev. Lett. **95**, 183002 (2005).

[12] B. Roth, J. C. J. Koelemeij, H. Daerr, and S. Schiller, Phys. Rev. A **74**, 040501(R) (2006).

[13] M. Tadjeddine and G. Parlant, Mol. Phys. **33**, 1797 (1977).

[14] A. Kondorskiy (private communication).

[15] J. C. J. Koelemeij, B. Roth, A. Wicht, I. Ernsting, and S. Schiller, Phys. Rev. Lett. **98**, 173002 (2007).

[16] D. Gerlich, in *Advances in Chemical Physics*, Vol. 82, Part 1, Experiment, edited by C.-Y. Ng and M. Baer (John Wiley and Sons, New York, 1992).

[17] D. J. Wineland, C. Monroe, W. M. Itano, D. Leibfried, B. E. King, and D. M. Meekhof, J. Res. Natl. Inst. Stand. Technol. **103**, 259 (1998).

[18] P. O. Schmidt, T. Rosenband, C. Langer, W. M. Itano, J. C. Bergquist, and D. J. Wineland, Science **309**, 749 (2005).

[19] J. K. Thompson, S. Rainville, and D. E. Pritchard, Nature (London) **430**, 58 (2004).

[20] G. Morigi and H. Walther, Eur. Phys. J. D **13**, 261 (2001).

[21] M. Barrett *et al.*, Phys. Rev. A **68**, 042302 (2003).

[22] D. Leibfried *et al.*, Nature (London) **422**, 412 (2003).

[23] R. Kepa, A. Kocan, M. Ostrowska-Kopec, I. Piotrowska-Domagala, and M. Zachwieja, J. Mol. Spectrosc. **228**, 66 (2004).

[24] P. Rosmus and H. Werner, Mol. Phys. **47**, 661 (1982).

[25] F. Diedrich, J. C. Bergquist, W. M. Itano, and D. J. Wineland, Phys. Rev. Lett. **62**, 403 (1989).

[26] L. Deslauriers, S. Olmschenk, D. Stick, W. K. Hensinger, J. Sterk, and C. Monroe, Phys. Rev. Lett. **97**, 103007 (2006).

[27] D. Kielpinski, B. E. King, C. J. Myatt, C. A. Sackett, Q. A. Turchette, W. M. Itano, C. Monroe, D. J. Wineland, and W. H. Zurek, Phys. Rev. A **61**, 032310 (2000).

[28] T. P. Heavner, S. R. Jefferts, E. A. Donley, J. H. Shirley, and T. E. Parker, IEEE Trans. Instrum. Meas. **54**, 842 (2005).

[29] T. Rosenband, W. M. Itano, P. O. Schmidt, D. B. Hume, J. C. J. Koelemeij, J. C. Bergquist, and D. J. Wineland, in Proceedings of the 20th European Frequency and Time Forum, Braunschweig, Germany, 2006 (unpublished), pp. 289–291.

[30] T. Becker, J. v. Zanthier, A. Y. Nevsky, C. Schwedes, M. N. Skvortsov, H. Walther, and E. Peik, Phys. Rev. A **63**, 051802(R) (2001).

[31] T. Schneider, E. Peik, and C. Tamm, Phys. Rev. Lett. **94**, 230801 (2005).

[32] R. Le Targat, X. Baillard, M. Fouché, A. Brusch, O. Tcherbakoff, G. D. Rovera, and P. Lemonde, Phys. Rev. Lett. **97**, 130801 (2006).

[33] U. Sterr, C. Degenhardt, H. Stoehr, C. Lisdat, H. Schnatz, J. Helmcke, F. Riehle, G. Wilpers, C. W. Oates, and L. Hollberg, C. R. Phys. **5**, 845 (2004).

[34] M. M. Boyd, A. D. Ludlow, S. Blatt, S. M. Foreman, T. Ido, T. Zelevinsky, and J. Ye, Phys. Rev. Lett. **98**, 083002 (2007).

[35] H. S. Margolis, G. P. Barwood, G. Huang, H. A. Klein, S. N. Lea, K. Szymaniec, and P. Gill, Science **306**, 1355 (2004).

[36] W. H. Oskay *et al.*, Phys. Rev. Lett. **97**, 020801 (2006).

[37] J. Uzan, Rev. Mod. Phys. **75**, 403 (2003).

[38] J. B. Schilling, W. A. Goddard III, and J. L. Beauchamp, J. Am. Chem. Soc. **109**, 5565 (1987).

[39] G. Ohanessian, M. J. Brusich, and W. A. Goddard III, J. Am. Chem. Soc. **112**, 7179 (1990).

[40] K. Sugiyama and J. Yoda, Phys. Rev. A **55**, R10 (1997).