Optical Pumping of Trapped Neutral Molecules by Blackbody Radiation

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Optical pumping by blackbody radiation is a feature shared by all polar molecules and fundamentally limits the time that these molecules can be kept in a single quantum state in a trap. To demonstrate and quantify this, we have monitored the optical pumping of electrostatically trapped OH and OD radicals by room-temperature blackbody radiation. Transfer of these molecules to rotationally excited states by blackbody radiation at 295 K limits the $1/e$ trapping time for OH and OD in the $X^2\Pi_{3/2}$, $v'' = 0$, $J'' = 3/2(f)$ state to 2.8 and 7.1 s, respectively.

In his 1917 paper Einstein showed [1] that even in the absence of collisions the velocity distribution of a molecular gas takes on a Maxwellian distribution due to the momentum transfer that takes place in the absorption and emission of blackbody radiation. The absorbed and emitted photons optically pump the rotational and vibrational transitions, resulting in thermal distributions over the available states. The rotational temperature of the CN molecule in interstellar space [2], for example, is the result of optical pumping by the cosmic microwave background-radiation [3].

The influence of blackbody radiation on atoms and molecules is in general small and it is rare that it can be observed directly in laboratory experiments. However, in a number of cases the interaction with blackbody radiation is experimentally observable and important. The first dynamical effects of blackbody radiation on the population of atomic levels were noticed when studying the lifetime of highly excited Rydberg states in atoms [4]. Atoms in these states can have dipole moments of thousands of Debye, and have sufficient spectral overlap with the spectrum of room-temperature blackbody radiation. The excitation (and ionization) rates can be on the order of 1000 s^{-1}, implying that the effect can already be observed on a μs time scale.

The excitation rates in ground state atoms and molecules are generally much lower, and therefore require a longer interaction time to be observed. Only with the development of ion traps, together with a sufficient reduction of collisional energy exchange (i.e., a good vacuum at room temperature), could the photodissociation of molecular ions and clusters by blackbody radiation be directly observed [5,6]. Ions in storage rings are also trapped long enough for the interaction with blackbody radiation to be noticeable [7].

The effect of blackbody radiation on neutral molecules in a trap has until now been left experimentally unexplored, partly because the conditions to observe the effect were not met, and partly because the importance of this effect was not always realized. Polar molecules generally have strong vibrational and/or rotational transitions in the infrared region of the spectrum. As a result they can relatively easily be optically pumped by room-temperature blackbody radiation, and this fundamentally limits the time that these molecules can be kept in a single quantum state in room-temperature traps. This has important implications for cooling schemes which aim at increasing the phase-space density of trapped neutral polar molecules.

In the rapidly growing research field of cold molecules, these polar molecules are of special interest. When quantum degeneracy is reached with polar molecules it will be much different from atomic Bose-Einstein condensates or degenerate Fermi gasses due to the dipole-dipole interaction [8,9]. Trapped polar molecules also hold promise for use in quantum information systems [10]. Furthermore a search for a permanent electric dipole moment of the electron, which would result in the violation of time reversal symmetry, is being done using polar molecules [11] because an external electric field applied to a polar molecule leads to a hugely magnified internal field. Quantum chemistry and collisions at low energy [12] are other examples of the possibilities with cold polar molecules.

Many of these exciting experiments require a dense and cold sample of trapped polar molecules. Therefore effort in the research on cold molecules is currently aimed at increasing the phase-space density of the trapped molecules [13]. A natural approach to try to reach this goal is to adapt the cooling techniques such as evaporative cooling [14] and sympathetic cooling [15], but these cooling techniques require usually trapping times of 10 s or more. Therefore an investigation of blackbody radiation as a limiting factor for the trapping time of polar molecules is of importance. Also for future studies of collisions between trapped molecules a quantitative understanding of all trap loss mechanisms is essential. In this Letter we experimentally quantify trap loss due to blackbody radiation for neutral polar molecules stored in a room-temperature trap, using the OH radical as a model system. Cold packets of OH radicals are produced using the Stark deceleration and trapping technique [16,17].

A natural approach to experimentally study the effect of blackbody radiation on the trapped molecules would be to vary the temperature of the trapping apparatus, thereby changing both the spectral distribution and the intensity of the blackbody radiation. A disadvantage of this is that normally a change of the temperature will also influence the vacuum conditions, changing the collision rate with the residual gas. The alternative approach we have taken is to compare the room-temperature trapping of two isotopic variants of the same molecule. Under the assumption that these isotopomers have the same collisional properties, the trap losses due to blackbody radiation and collisions with background gas can be disentangled.

The molecules we have compared are the OH and OD radical. There is sufficient intensity in the low-energy side of the blackbody radiation spectrum that these molecules can be rotationally excited; the vibrational energy splitting is so large that vibrational excitation is negligible. The energies of the relevant rotational states of OH and OD in the $X^2\Pi$ state are depicted in Fig. 1. Each rotational level is split into two Λ-doublet components with opposite

parity, denoted by f and e. In an electric field these components are mixed. In the electric field, each J state is split into $(2J + 1)$ $M_J\Omega$ components. The f component in zero field corresponds with $(2J + 1)/2$ low-field seeking components in an electric field; the e component corresponds with $(2J + 1)/2$ high-field seeking components.

Blackbody radiation can excite transitions with $\Delta M_J = \pm 1, 0$. Molecules trapped in low-field seeking states can be pumped to high-field seeking states, leading to trap loss. Because the rotational constant B is almost a factor of 2 larger for OH than for OD, the intensity of the room-temperature blackbody radiation is much higher at the excitation energy of the first rotational excitation for OH molecules than it is for OD molecules. The most important transition rates due to the blackbody radiation connecting the f components of the lowest rotational levels are indicated next to the arrows in Fig. 1. The difference in the excitation rates leads us to expect significantly shorter trapping times for OH than for OD radicals.

The production, deceleration, and trapping of OH has already been described elsewhere [18]; here we summarize the main procedure. The experimental setup is schematically depicted in Fig. 2. The OH (OD) radicals are created, in separate experiments, by photodissociation of HNO_3 (DNO_3), coexpanded with xenon as a carrier gas in a pulsed supersonic expansion. After the expansion both OH and OD are mostly in the electronic, vibrational, and rotational ground state $X^2\Pi_{3/2}$ ($v = 0$, $J = 3/2$). The $M_J\Omega = -9/4$ component of the $3/2(f)$ state is the strongest low-field-seeking state and is focused by a hexapole lens into the decelerator. Using 108 deceleration stages a
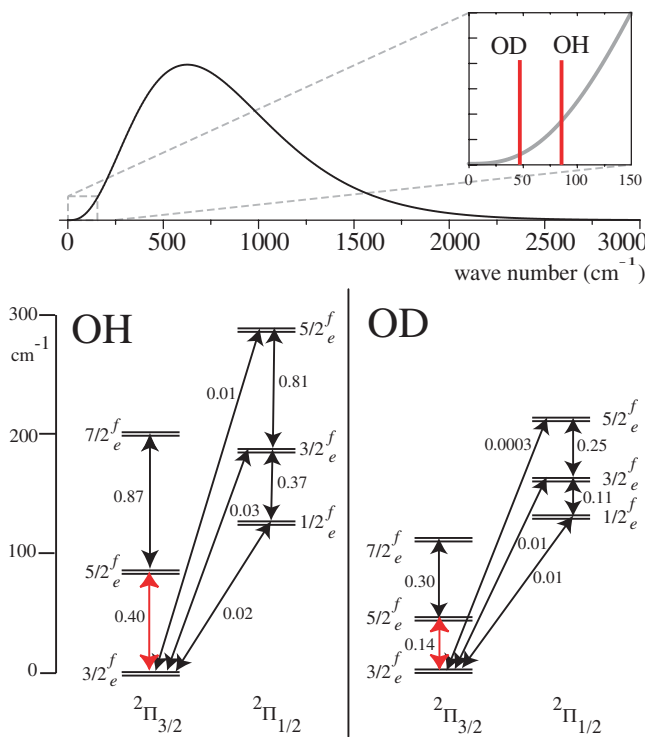

FIG. 1 (color online).   In the upper part, the room-temperature spectrum of blackbody radiation is shown. The relevant region for rotational excitation of OH and OD radicals is shown, with sticks indicating the lowest rotational excitation frequency. In the lower part the relevant rotational levels of OH and OD are depicted. Each rotational level is split into two Λ-doublet components with opposite parity, denoted by f and e. The size of the splitting is exaggerated for clarity. The most relevant transition rates (in s^{-1}) due to blackbody radiation connecting the f components of rotational levels are indicated next to the arrows.
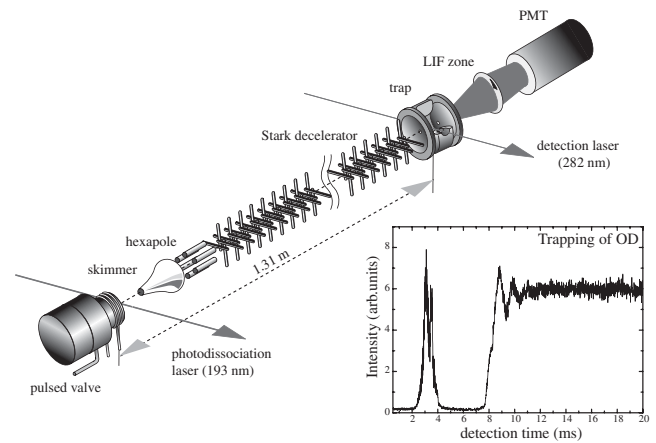

FIG. 2.   Scheme of the experimental setup. OH (OD) radicals are created by photodissociation of supersonically expanded (deuterated) nitric acid, and subsequently decelerated in a Stark decelerator. The slowed molecules are trapped in an electrostatic trap, and the population in the different rotational states is probed by laser-induced fluorescence detection. In the inset the arrival of undecelerated OD molecules followed by the steady signal of the trap-loaded OD molecules is shown, up to 20 ms after production of the molecules. We have detected the trapped molecules up to 15 s.

part of the beam is brought to a standstill, and subsequently trapped in an electrostatic quadrupole trap. In these experiments the OD radical, which is predicted to have interesting collisional properties [19], has been trapped for the first time. Because of their similar mass and dipole moment OH and OD are equally well decelerated and trapped. We estimate the trapped number density to be about 10^7 molecules/cm^3, and have not found any indication of collisions between the trapped molecules. The trapped molecules, probed by laser-induced fluorescence directly after switching off the trapping voltages, are initially exclusively in the $M_J \Omega = -9/4$ component of the $3/2(f)$ state.

We have measured, for OH and OD, the population trapped in the $3/2(f)$ state, up to a trapping time of 15 s. The results are shown in the upper part of Fig. 3. The OD molecules remain, as expected, approximately a factor of 2 longer in the $3/2(f)$ state than the OH molecules. To interpret the data we have used a rate-equation model, describing the time evolution of the population in the rotational states. The curves in Fig. 3 show the outcome of this model. Molecules can be pumped from the $3/2(f)$ state to the $5/2(f)$ state, in which they can remain trapped. The time evolution of the $5/2(f)$ population follows from

the rate-equation model. The results of the measurement of the population in this state are shown in the lower part of Fig. 3. About 5% of the original OD population accumulates in the $5/2(f)$ state after 3 s of trapping. For OH the maximum in the $5/2(f)$ population occurs after 1 s of trapping. From the $5/2(f)$ state the molecules can be pumped to other rotational states again, spontaneously decay back to the $3/2(f)$ state, or be lost due to collisions with the background gas.

For the model, the transition strengths of all allowed transitions between the M_J components of the rotational states (for both Ω manifolds, up to $J = 7/2$) in OH and OD are calculated. The energy differences caused by hyperfine effects, the Stark shift of the levels in the electric field of the trap, and the Λ-doubling itself are so small compared to the rotational spacing that these are neglected in the calculation of the transition rates. Using the calculated transition strengths and the spectrum of the blackbody radiation at 295 K the transition rates due to the blackbody radiation are obtained, as shown in Fig. 1. Because not all M_J components have an equal Stark shift the different trapping depths for these states were taken into account. Molecules excited to the $J \geq 7/2$ states are considered lost from the trap. Stimulated emission was also included. Loss due to collisions with residual background gas, assumed to be independent of the rotational level, is taken into account by a constant loss rate. We find best agreement between the model and the data using a background-gas loss rate of 0.17 s^{-1} [20]. To verify whether this loss rate can be explained by collisions with a xenon background gas we have used the recently calculated cross section for Xe-OH collisions [12], taken to be identical for OH and OD. For a room-temperature gas of xenon atoms colliding with trapped OH molecules the average collision energy is 30 cm^{-1}, leading to an elastic cross section of 500 ± 50 Å^2; rotational excitation of trapped OH and OD by the xenon atoms can safely be neglected. Because the trap depth is only about 1 cm^{-1} almost every collision will lead to trap loss. Using a partial xenon pressure of 5×10^{-9} mbar we find a collision rate of 0.14 s^{-1}, which is consistent with the rate found from the comparison of the model with the data.

We have calculated the blackbody pumping rates for a number of other polar molecules as well. These molecules are well suited for trapping, using the various currently available techniques [13]. For the selected molecules the blackbody pumping rate out of the specified initial quantum state is compared, for two different temperatures, in Table I. The initial state is in most cases the electronic, vibrational, and rotational ground state. The rate for OH is slightly larger than the sum of the rates indicated in Fig. 1 due to the effect of hyperfine structure that was included in these calculations.

The room-temperature pumping rate for many of the listed molecules is comparable to that of OH and OD. LiH, with its favorable Stark effect to mass ratio and the
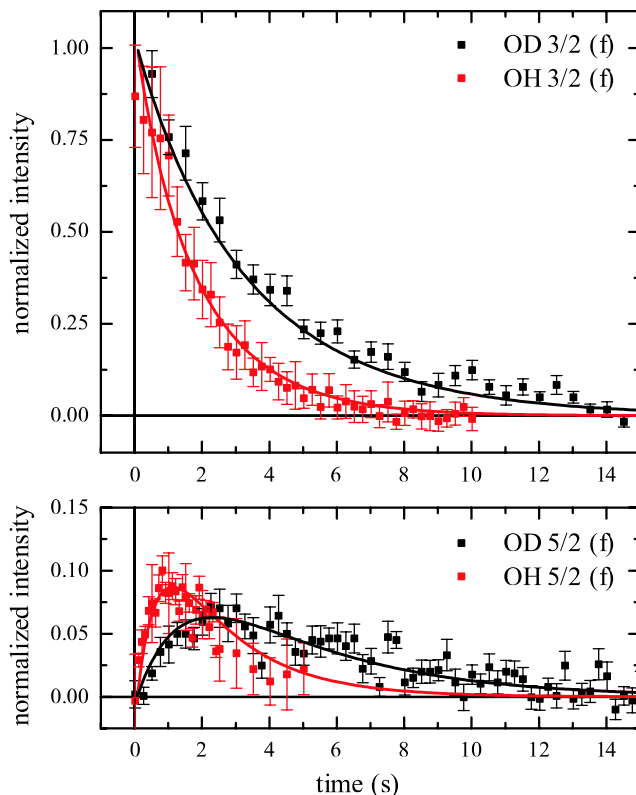

FIG. 3 (color online). The population of electrostatically trapped OH and OD radicals in the $3/2(f)$ and $5/2(f)$ levels as a function of time. The squares are the measured data: red (gray) for OH, black for OD. The curves are the outcome of the rate-equation model using a constant background-gas collision rate of 0.17 s^{-1}.

TABLE I.   Pumping rates due to blackbody radiation at two different temperatures, out of the specified initial state, for a number of polar molecules.

System	Initial state	Pumping rate (s^{-1})	
		295 K	77 K
OH/OD	$X^2\Pi_{3/2}, J = \frac{3}{2}$	0.49/0.16	0.058/0.027
NH/ND	$a^1\Delta, J = 2$	0.36/0.12	0.042/0.021
NH/ND	$X^3\Sigma^-, N = 0, J = 1$	0.12/0.036	0.025/0.0083
NH$_3$/ND$_3$	$\tilde{X}^1A_1', J = 1, \|K\| = 1$	0.23/0.14	0.019/0.0063
SO	$X^3\Sigma^-, N = 0, J = 1$	0.01	$<10^{-3}$
^{6}LiH/^{6}LiD	$X^1\Sigma^+, J = 1$	1.64/0.81	0.31/0.11
CaH/CaD	$X^2\Sigma^+, N = 0, J = \frac{1}{2}$	0.048/0.063	0.0032/ $< 10^{-3}$
RbCs	$X^1\Sigma^+, J = 0$	$<10^{-3}$	$<10^{-3}$
KRb	$X^1\Sigma^+, J = 0$	$<10^{-3}$	$<10^{-3}$
CO	$a^3\Pi_{1,2}, J = 1, 2$	0.014/0.014	$<10^{-3}/ < 10^{-3}$

existence of 4 isotopomers often considered an ideal candidate molecule [21], is especially sensitive to blackbody radiation: even at 77 K it can only be trapped for a few seconds. At 4 K the rates for all molecules are smaller than 10^{-3}. Depending on the molecule the pumping rate is either dominated by rotational transitions (OH/OD, NH/ND, LiH/LiD), by vibrational transitions (CO, RbCs, KRb), or by a combination of both. CO, RbCs, and KRb have very small blackbody pumping rates.

In this Letter we have experimentally studied trap loss of neutral polar molecules due to room-temperature blackbody radiation, using the OH radical as a model system. By comparing the trapping times of OH and OD radicals in an electrostatic quadrupole trap, the individual contribution of blackbody radiation and collisions with background gas could be quantified. Loss due to blackbody radiation is a major limitation for the room-temperature trapping of OH and OD radicals. If the vacuum conditions were improved such that losses due to collisions with background gas were completely removed, the $1/e$ trapping time would increase to 7.1 s for OD and 2.8 s for OH. The trapped molecules will have to be shielded from thermal radiation if longer trapping times are required. We have shown that these limitations are shared by a large class of polar molecules, which has profound consequences for the implementation of further cooling schemes.

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