Direct Measurement of the Radiative Lifetime of Vibrationally Excited OH Radicals

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Neutral molecules, isolated in the gas phase, can be prepared in a long-lived excited state and stored in a trap. The long observation time afforded by the trap can then be exploited to measure the radiative lifetime of this state by monitoring the temporal decay of the population in the trap. This method is demonstrated here and used to benchmark the Einstein A coefficients in the Meinel system of OH. A pulsed beam of vibrationally excited OH radicals is Stark decelerated and loaded into an electrostatic quadrupole trap. The radiative lifetime of the upper Λ-doublet component of the $X\,^2\Pi_{3/2}$, $v = 1$, $J = 3/2$ level is determined as 59.0 ± 2.0 ms, in good agreement with the calculated value of 58.0 ± 1.0 ms.

Infrared absorption and emission spectroscopy has a long and rich history in the development and application of molecular physics. Absorption and emission of infrared radiation is an important diagnostic means in determining the presence and concentration of molecular species in various environments, ranging from plasmas and flames to the Earth's atmosphere and interstellar space. A quantitative analysis of these observations relies on a detailed knowledge of the Einstein A coefficients that characterize the spontaneous emission rates. These A coefficients can generally be inferred from absorption measurements, provided the (line-integrated) number density and the temperature of the absorbing species are accurately known. The unstable nature of many chemically highly relevant molecules severely limits the accuracy of this approach for these species, however. The most direct and generally applicable route to accurately determining the A coefficients is to measure the radiative lifetimes of individual rovibrational levels. Molecules isolated in the gas phase and at low densities are needed for this, as interactions with a medium and quenching by collisions have to be avoided. The preferred way to measure the radiative lifetime is to prepare molecules in the quantum state of interest, and to measure the state-specific population as a function of time. The problem with this approach is that infrared radiative lifetimes are typically in the millisecond to second range, much longer than the observation times that are commonly available in experiments. Ingenious schemes have been developed that nevertheless enable a measurement of long radiative lifetimes of neutral molecules in a molecular beam [1,2]. Only for lifetimes up to a few milliseconds has it been possible to measure the population decay directly [3].

For charged particles, the greatly enhanced observation times that became available when traps were developed opened up the possibility to directly measure radiative lifetimes of metastable states [4]. For neutral atoms and neutrons, trapping has been used to directly measure long lifetimes as well [5]. Methods to confine neutral gas-phase molecules in magnetic [6], optical [7], and electrostatic traps [8] for times up to seconds have recently been developed. In this Letter we report on the first direct measurement of the infrared radiative lifetime of a vibrationally excited trapped molecule. By measuring the temporal decay of the population of OH ($X\,^2\Pi_{3/2}$, $v = 1$, $J = 3/2$) radicals in an electrostatic trap, an accurate value for the A coefficient of the fundamental 1-0 band of OH is obtained.

The infrared radiative properties of the OH radical are of particular importance. Vibrationally excited OH ($X\,^2\Pi$, $v \leq 9$) radicals, produced in the upper atmosphere via the reactive depletion of ozone [9,10], are responsible for the near-infrared nighttime air glow [11]. Recently, this OH Meinel band emission has also been observed from artificial auroras at higher altitudes, offering new possibilities to study ionospheric interactions [12]. OH vibrational emission has also been observed from stellar and interstellar space [13]. The so-called "prompt emission" in the 1-0 band of the OH radical (about 3.3 μm), produced by photodissociation of water, is used as a tracer for water produced in comets [14]. The radiative lifetimes of the vibrational states of OH ($X\,^2\Pi$) are essential for a quantitative interpretation of all these observations, and have therefore received considerable experimental and theoretical attention. Over the years, the values have scattered over a wide range and have only slowly converged [15]. The most recent values for the lifetimes, based on experimental absorption line intensities, are given in the HITRAN 2004 database [16]. For the $X\,^2\Pi_{3/2}$, $v = 1$, $J = 3/2$ level of OH, this database gives a lifetime of 56.6 ms with an error of 10%–20%.

The experiments are performed in a molecular beam deceleration and trapping machine that is schematically shown in Fig. 1. The same setup has been used recently for
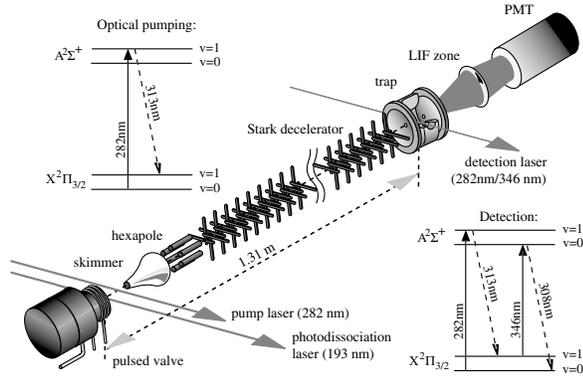
FIG. 1.   Scheme of the experimental setup. A pulsed beam of OH ($v = 0$) radicals is produced via photodissociation (193 nm) of HNO_3 molecules seeded in Xe. Prior to entering the decelerator, part of the OH radicals are prepared in the $v = 1$ state by Franck-Condon pumping via the $A\,^2\Sigma^+$ state (upper left). OH radicals in the $J = 3/2$ level of both the $v = 0$ and the $v = 1$ vibrational states of the $X\,^2\Pi_{3/2}$ electronic ground state are Stark decelerated and subsequently loaded into the electrostatic trap. Molecules in the trap are state-selectively detected by imaging the laser induced fluorescence onto a PMT.

the experimental demonstration of the electrostatic trapping of OH ($X\,^2\Pi_{3/2}$, $v = 0$) radicals [17]. A pulsed beam of OH radicals with a mean velocity of 360 m/s is produced via ArF-laser dissociation of HNO_3, seeded in Xe, near the orifice of a pulsed solenoid valve. In the experiments, the population in the $J = 3/2$ rotational level of the $v = 0$ and $v = 1$ vibrational states of the $X\,^2\Pi_{3/2}$ electronic ground state is of relevance. During the expansion, most of the OH radicals cool down to the rovibrational ground state $v = 0$, $J = 3/2$. Just after the expansion region, approximately 15% of the OH ($v = 0$) radicals are promoted to the $X\,^2\Pi_{3/2}$, $v = 1$ state by Franck-Condon pumping via the $A\,^2\Sigma^+$ state at 282 nm [18]. This optical pumping scheme is shown in the upper left of Fig. 1. In the presence of an electric field, the upper Λ-doublet components of the $J = 3/2$ levels split into a low-field seeking $M_J\Omega = -3/4$ and a $M_J\Omega = -9/4$ component. Only OH radicals in the $J = 3/2$, $M_J\Omega = -9/4$ component of either vibrational state are Stark decelerated and subsequently loaded into the quadrupole trap.

After passage through a 2 mm diameter skimmer, the beam enters the deceleration chamber, and is focused into the Stark decelerator by a short hexapole. The operation principles of the hexapole, Stark decelerator, and quadrupole trap are given elsewhere [17]. Briefly, the Stark decelerator exploits the interaction of polar molecules with time-varying electric fields to reduce the velocity of the molecular beam in a stepwise fashion. The 1.18 m long decelerator consists of an array of 108 electric field stages that are placed 11 mm apart. Each field stage consists of

two 6 mm diameter parallel electrodes, centered 10 mm apart, that are oriented perpendicular to the molecular beam axis. Adjacent electric field stages are rotated by 90° with respect to each other to provide a 4×4 mm^2 transverse area for the beam to pass. When at the appropriate times a voltage difference of 40 kV is applied between the electrodes of the electric field stages, OH radicals in the $J = 3/2$, $M_J\Omega = -9/4$ component are decelerated from 360 to 20 m/s. The Stark shifts of the $v = 0$ and 1 states of OH are very similar [19], and molecules in both vibrational states are simultaneously decelerated and loaded into the quadrupole trap with equal efficiency. The trap consists of a ring electrode and two hyperbolic end caps, and is located 21 mm downstream from the decelerator. The trap is mounted in a separate differentially pumped vacuum chamber, where the pressure does not exceed 2×10^{-9} mbar under operating conditions. Depending on the voltages that are applied to the trap electrodes, either a last deceleration stage or a (nearly) symmetric 500 mK deep potential well can be created. The OH radicals enter the trap through a 4 mm diameter hole in the first end cap, and come, approximately 8 ms after their production, to a standstill near the center of the trap. At this time, the voltages on the trap electrodes are switched to confine the OH radicals in the potential well. The density of OH radicals at the center of the trap is measured using laser induced fluorescence (LIF) detection schemes, shown in the lower right of Fig. 1. The population of the OH radicals in the $v = 0$, $J = 3/2$ and $v = 1$, $J = 3/2$ levels is state-selectively probed by inducing the $Q_1(1)$ transitions of the $A\,^2\Sigma^+$, $v = 1 \leftarrow X\,^2\Pi$, $v = 0$ band about 282 nm and the $A\,^2\Sigma^+$, $v = 0 \leftarrow X\,^2\Pi$, $v = 1$ band about 346 nm, respectively. The off-resonant fluorescence about 313 nm (when probing $v = 0$) and 308 nm (when probing $v = 1$) is imaged through a 6 mm diameter opening in the second end cap onto a photomultiplier tube (PMT). Stray light from the laser is largely avoided by using light baffles and is suppressed by optical filters in front of the PMT.

In Fig. 2, the LIF signal of the trapped cloud of OH radicals in the $v = 0$, $J = 3/2$ level (upper curve) and in the $v = 1$, $J = 3/2$ level (lower curve) is shown as a function of the storage time t. The trapping potential is switched on at $t = 0$ ms. The experiment runs at a repetition rate of 5 Hz to allow for a maximum observation time of (almost) 200 ms in the trap. On this time scale, OH radicals in the $v = 0$ state mainly leave the trap via collisions with background gas; both elastic and inelastic collisions with the thermal background gas transfer an amount of kinetic energy to the OH radicals that largely exceeds the trap depth. From a separate series of measurements, running the apparatus at lower repetition rates while maintaining the same background pressure, a $1/e$ trap lifetime of 1.3 ± 0.1 s is deduced. The population of trapped OH radicals in the $v = 1$ state, on the other hand, is mainly depleted via spontaneous emission to the $v = 0$ state, in
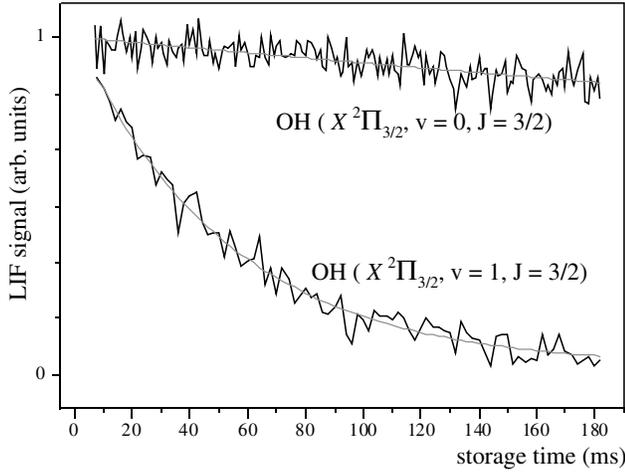
FIG. 2. Population of trapped OH radicals in the $X\,^2\Pi_{3/2}$, $v = 0$, $J = 3/2$ level (upper curve) and in the $X\,^2\Pi_{3/2}$, $v = 1$, $J = 3/2$ level (lower curve), as a function of the storage time t. The trapping potential is switched on at $t = 0$ ms.
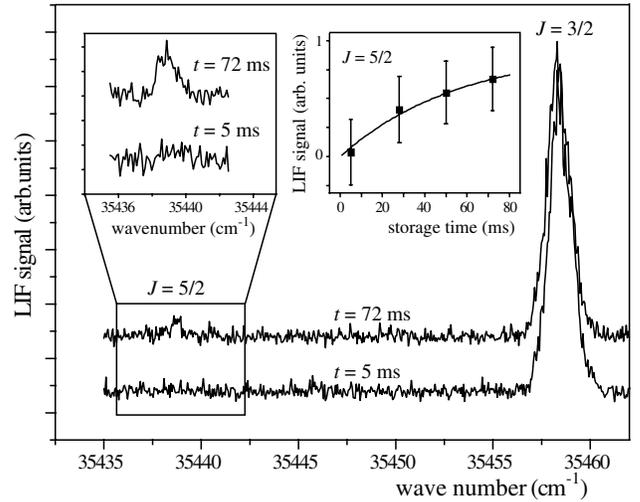

FIG. 3. Excitation spectrum of trapped OH ($v = 0$) radicals that is recorded 5 ms (lower curve) and 72 ms (upper curve) after switching on the trap. In the central inset, the population of trapped OH radicals in the $v = 0$, $J = 5/2$ level is shown as a function of the storage time.

addition to collisions with background gas. The observed exponentially decaying curve therefore almost directly reflects the radiative lifetime of the $X\,^2\Pi_{3/2}$, $v = 1$, $J = 3/2$ level of OH. From a series of measured decay curves, taking carefully the baseline and the signal-to-noise ratio of the LIF signal into account, an exponential decay time of 56.4 ± 1.9 ms is deduced. The inherent trap lifetime can be assumed to be identical for OH radicals in the $v = 0$ and 1 vibrational states, as the total collision cross sections with thermal background gas will be very similar for OH in either one of the vibrational states. Under this assumption, a radiative lifetime τ for OH radicals in the upper Λ-doublet component of the $X\,^2\Pi_{3/2}$, $v = 1$, $J = 3/2$ level of $\tau = 59.0 \pm 2.0$ ms is obtained. In a nondecelerated beam of OH radicals that passes through the trap about 3.6 ms after production, the population of OH radicals in the $v = 2$ state is measured to be more than an order of magnitude less than the population in the $v = 1$ state. Repopulation of the $v = 1$ state in the trap via cascading spontaneous emission from higher vibrational states is therefore negligible in our experiment.

OH radicals in the $v = 1$, $J = 3/2$ level that are confined in the trap undergo infrared spontaneous emission to the $v = 0$ state, following the selection rules of the electric dipole allowed transitions in the presence of an electric field. The molecules can make a transition to all $M_J\Omega$ components of the $J = 1/2, 3/2$, and $5/2$ rotational levels of the $X\,^2\Pi$, $v = 0$ electronic ground state. Of these, only molecules that end up in the $M_J\Omega = -15/4, -9/4$, and $-3/4$ components of the $J = 5/2$ level or in the $M_J\Omega = -9/4$ and $-3/4$ components of the $J = 3/2$ level are (partially) recaptured and confined in the trap. In Fig. 3, the excitation spectrum of trapped OH ($v = 0$) radicals is shown that is recorded 5 ms (lower curve) and 72 ms

(upper curve) after switching on of the trap. The detection laser is scanned over the $Q_1(1)$ and $Q_1(2)$ transitions of the $A\,^2\Sigma^+$, $v = 1 \leftarrow X\,^2\Pi_{3/2}$, $v = 0$ band, probing the population in the $v = 0$, $J = 3/2$ and $v = 0$, $J = 5/2$ levels, respectively. Initially, the trapped OH $v = 0$ radicals exclusively reside in the $J = 3/2$ level, the only rotational state that is selected by the Stark decelerator. After 72 ms of trapping, a small but significant population of OH radicals in the $v = 0$, $J = 5/2$ level is detected in the trap. In the central inset of Fig. 3, the accumulation over time of the trapped OH ($v = 0$, $J = 5/2$) radicals is shown. The expected exponential growth of the population in the $J = 5/2$ level, as deduced from the measurements shown in Fig. 2, is shown as well. The relative population of trapped OH radicals in the $v = 0$, $J = 3/2$ and $v = 0$, $J = 5/2$ levels is also consistent with the expectations. An overall factor of about 20 is expected, based on the initial relative population of $v = 0$ and 1 in the trap and the Hönl-London factor for fluorescence from the $v = 1$, $J = 3/2$ to the $v = 0$, $J = 5/2$ level, in combination with the larger size of the trapped cloud of $J = 5/2$, e.g., the reduced overlap with the detection laser.

The radiative properties of the OH radical can be calculated from its dipole moment function and the potential energy curve. The radiative lifetime τ of the upper Λ-doublet component [of $f(+)$ parity] of the $X\,^2\Pi_{3/2}(v = 1, J = 3/2)$ level of OH is given by

$$\tau^{-1} = \sum_f A^{fi} = \sum_f \frac{4\alpha\omega_{fi}^3}{3c^2e^2}|\langle f|\mu|i\rangle|^2, \qquad (1)$$

where A^{fi} are the Einstein A coefficients for the $X\,^2\Pi$, $v = 1 \rightarrow X\,^2\Pi$, $v = 0$ transitions, α is the fine structure con-

stant, ω_{fi} the angular frequency of the emitted photon, c the speed of light, and e the elementary charge. In the calculation of the initial ($|i\rangle$) and final ($|f\rangle$) states, Λ-type doubling and spin-orbit, spin-rotation, and rotation-vibration coupling is taken into account. The sum over the final states includes all spin-orbit levels with $J \leq 5/2$. The $X^2\Pi$ potential energy curve and the r-dependent dipole moment μ are obtained from an internally contracted multireference configuration interaction calculation with the MOLPRO [20] program package. Special relativistic effects are taken into account by using Douglas-Kroll one-electron integrals. The molecular orbitals are obtained from a 1σ–5σ, 1π–2π complete active space self-consistent field calculation, employing an augmented correlation consistent polarized valence 6-zeta (aug-cc-pV6Z) one-electron basis set. The r-dependent spin-orbit couplings are obtained in a similar calculation employing an uncontracted aug-cc-pVQZ basis. The Λ-type doubling parameters are taken from spectroscopic observations [21]. The result that is obtained for the radiative lifetime in the presence of a full parity mixing electric field is $\tau = 58.0$ ms (in field-free conditions $\tau = 57.7$ ms), in good agreement with the experimentally determined value. As the computed rovibrational energy levels agree with experiments to better than 0.02% and as our dipole moments agree with previous high level *ab initio* calculations [22] to about 0.7%, we estimate the error in τ to be about 1 ms.

In this Letter, we report the first direct measurement of the quantum-state-specific infrared radiative lifetime of a trapped molecule. The technique reported here can generally be applied to directly measure lifetimes of metastable states of neutral molecules up to seconds, with an unprecedented accuracy. A requirement is that it must be possible to confine the molecules in the desired quantum state in a trap. The molecules can be prepared in the metastable state prior to deceleration and trapping, as reported here. Alternatively, they can first be trapped in the quantum state that is best suited for it, and preparation of the desired metastable state can then be performed inside the trap. By recording the decay of the population of vibrationally excited OH ($X^2\Pi_{3/2}$, $\nu = 1$, $J = 3/2$) radicals in an electrostatic quadrupole trap, the radiative lifetime of this level is determined as 59.0 ± 2.0 ms, in good agreement with the theoretically predicted value of 58.0 ± 1.0 ms. This provides a benchmark for the Einstein A coefficients in the Meinel system of OH. This is of particular importance in, for instance, combustion, atmospheric science, and astrophysics.

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