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Direct Measurement of the Radiative Lifetime of Vibrationally Excited OH Radicals

Sebastiaan Y. T. van de Meerakker,1,2 Nicolas Vanhaecke,1 Mark P. J. van der Loo,3 Gerrit C. Groenenboom,3 and Gerard Meijer1

1Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
2FOM-Institute for Plasmaphysics Rijnhuizen, Edisonbaan 14, 3439 MN Nieuwegein, The Netherlands
3Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

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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 A-doublet component of the $X^2Π_{3/2}$, $ν = 1$, $J = 3/2$ level is determined as $59.0 ± 2.0$ ms, in good agreement with the calculated value of $58.0 ± 1.0$ ms.

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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 ($X^2Π_{3/2}$, $ν = 1$, $J = 3/2$) 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 ($X^2Π$, $ν = 9$) 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 ($X^2Π$) 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 $X^2Π_{3/2}$, $ν = 1$, $J = 3/2$ 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...
that are placed 11 mm apart. Each field stage consists of a decelarator consists of an array of 108 electric field stages to reduce the velocity of the molecular beam in a stepwise fashion. The 1.18 m long time-varying electric fields to reduce the velocity of the 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 \( v = 1 \) 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 (\( v = 0 \)) radicals is produced via photodissociation (193 nm) of HNO3 molecules seeded in Xe. Prior to entering the decelerator, a pulsed valve switches on at time \( t = 0 \) 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 \( 1.3 \pm 0.1 \) 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

![Diagram](https://example.com/diagram.png)

**FIG. 1.** Scheme of the experimental setup. A pulsed beam of OH (\( v = 0 \)) radicals is produced via photodissociation (193 nm) of HNO3 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. OH radicals in the \( J = 3/2 \) level of both the \( v = 0 \) and \( v = 1 \) vibrational states of the \( X^2 \Pi_{3/2} \) electronic ground state are Stark decelerated and subsequently loaded into the quadrupole trap. Molecules in the trap are state-selectively detected by imaging the laser induced fluorescence onto a PMT.
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either one of the vibrational states. Under this assumption,
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vibrational states, as the total collision cross sections
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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 \( 56.4 \pm 1.9 \text{ ms} \) 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 \( \tau \) for OH radicals in the upper
\( \Lambda \)-doublet component of the \( X^2\Pi_{3/2}, v = 1, J = 3/2 \) level of \( \tau = 59.0 \pm 2.0 \text{ ms} \) is obtained. In a nondeceler-
ated 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 \( v = 1, J = 3/2 \) that are con-
fined 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 \( M_f \Omega \)
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 \( M_f \Omega = -15/4, -9/4, \) and
\(-3/4 \) components of the \( J = 5/2 \) level or in the \( M_f \Omega =
-9/4 \) 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 \( Q_{3/2}(1) \) and \( Q_{5/2}(2) \) transitions of
the \( A^2\Sigma^+, J = 1 \leftrightarrow X^2\Pi_{3/2}, v = 0 \) 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 ex-
clusively 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 Hön-
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 calcu-
lated from its dipole moment function and the potential
energy curve. The radiative lifetime \( \tau \) of the upper
\( \Lambda \)-doublet component \( [f(+) \text{ parity}] \) of the \( X^2\Pi_{3/2}(v =
1, J = 3/2) \) level of OH is given by
\[
\tau^{-1} = \sum_f A_{fi} = \frac{4\alpha c^2}{3} \sum_f \frac{4\alpha c^2}{3} |\langle f|\mu|i\rangle|^2, \tag{1}
\]
where \( A_{fi} \) are the Einstein \( A \) coefficients for the \( X^2\Pi, v =
1 \leftrightarrow X^2\Pi, v = 0 \) transitions, \( \alpha \) is the fine structure con-

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 \( t = 0 \text{ ms} \).

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.
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 ($X^2\Pi_{3/2}$, $v = 1$, $J = 3/2$) 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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