The radiative lifetime of metastable CO ($a\,^3\Pi$, $v=0$)

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We present a combined experimental and theoretical study on the radiative lifetime of CO in the $a\,^3\Pi_{1,2}$, $v=0$ state. CO molecules in a beam are prepared in selected rotational levels of this metastable state, Stark-decelerated, and electrostatically trapped. From the phosphorescence decay in the trap, the radiative lifetime is measured to be 2.63 ± 0.03 ms for the $a\,^3\Pi_1$, $v=0$, $J=1$ level. From the spin-orbit coupling between the $a\,^3\Pi$ and the $A\,^1\Pi$ states a 20% longer radiative lifetime of 3.16 ms is calculated for this level. It is concluded that coupling to other $^1\Pi$ states contributes to the observed phosphorescence rate of metastable CO. *© 2007 American Institute of Physics*. [DOI: 10.1063/1.2813888]

Triggered by the observation of CO in the upper atmosphere of Mars with a UV spectrometer on board the Mariner 6 spacecraft in 1969,[1] researchers started studying the UV bands of CO in increasing detail. In particular, the $a\,^3\Pi \leftarrow X\,^1\Sigma^+$ transition between the ground state and the lowest electronically excited state of CO, the so-called Cameron bands, became the subject of theoretical as well as experimental interest. From the appearance of the spectrum it was concluded that the intensity in this spin-forbidden transition mainly originates from spin-orbit mixing of the $a\,^3\Pi$ state with $\mathrm{a}^1\Pi$ state; a detailed analysis revealed that mixing of $^1\Sigma$ states with the $a\,^3\Pi$ state contributes less than 1% to the total intensity.[2] Using perturbation theory and taking only the interaction with the $A\,^1\Pi$ state into account, James calculated the radiative lifetimes for various rovibrational levels in the $a\,^3\Pi$ state.[3] These lifetimes are strongly J-dependent, but the ratio of the lifetimes of different J-levels is known with spectroscopic accuracy. The $J=1$ level in the $a\,^3\Pi_1$, $v=0$ manifold, from now on indicated as the $(\Omega,v,J)=(1,0,1)$ level, has the shortest lifetime, calculated by James as 2.93 ms; the (2,0,2) level, for instance, lives 54.66 times longer.

An accurate experimental value for the radiative lifetime of rovibrational levels of metastable CO is a benchmark for theoretical calculations on spin-orbit mixing of electronically excited states as well as on transition dipole moments. It has proved to be difficult, however, to experimentally determine the lifetime of any of the levels of the $a\,^3\Pi$ state of CO accurately.[4–7] These lifetimes can either be extracted from absorption measurements on the Cameron bands or, more directly, from measurements of the phosphorescence decay. For absorption measurements, experimental parameters such as the line-integrated number density of ground-state CO molecules in a certain rovibrational level together with the absorption line-shape and the spectral profile of the light source have to be accurately known. It is more problematic that the Franck-Condon factors for the vibrational bands of this transition also have to be known to be able to deduce a radiative lifetime. For phosphorescence decay measurements, on the other hand, the rovibrational state distribution of the metastable molecules needs to be known, and, on the timescale of the phosphorescence, collisions need to be avoided. To achieve this, laser excitation of CO to single rovibrational levels of the metastable state in the collision-free environment of a molecular beam has been used.[8–10] An intrinsic problem in these molecular beam experiments is, however, that the molecules move with a high speed, typically limiting the time during which the phosphorescence can be detected to a fraction of a millisecond.

The Stark deceleration of a beam of polar molecules followed by electrostatic trapping enables the observation of state-selected molecules for several seconds.[11] Recently, the radiative lifetime of vibrationally excited OH radicals was determined by recording the temporal decay of their population in the trap.[12] Here we report the Stark deceleration and electrostatic trapping of metastable CO molecules that are laser prepared in either the (1,0,1) or in the (2,0,2) level. The radiative lifetimes are measured by monitoring the phosphorescence decay of the trapped molecules. Calculations to rationalize the observed lifetimes are presented.

The Stark deceleration of metastable CO molecules has been described in detail before.[13] In the present experiment, we use a Stark decelerator with 108 electric field stages to load the metastable CO molecules in an electrostatic trap. The experimental setup is schematically shown in Fig. 1. A pulsed beam of CO molecules with a mean velocity of 320 m/s is produced by expanding a mixture of 20% CO in Xe from a cooled pulsed valve ($T=203$ K). A packet of CO molecules in the upper (low-field seeking) Λ-doublet component of the (1,0,1) or (2,0,2) level in the metastable $a\,^3\Pi$

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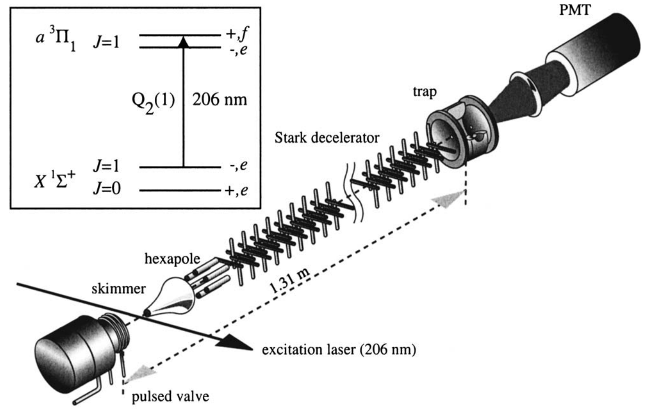

FIG. 1. Scheme of the experimental setup. A pulsed beam of CO molecules, laser prepared in either the (1,0,1) level (excitation scheme given in the inset) or the (2,0,2) level, is slowed down in the Stark decelerator and stored in an electrostatic trap. The phosphorescence to the electronic ground state is measured by a photomultiplier tube (PMT).

state is prepared by direct laser excitation from the $X\,^1\Sigma^+$, $v=0$ ground state. After passing through a skimmer, the packet of molecules is slowed down in the Stark decelerator and subsequently loaded and confined in an electrostatic quadrupole trap. When in the (1,0,1) level, about 10^5 CO molecules are trapped at a density of $10^8/\text{cm}^3$ and at a temperature of around 20 mK; in the (2,0,2) level an order of magnitude less molecules are trapped at a somewhat higher temperature. A detailed description of the Stark decelerator and of the electrostatic trap that have been used can be found elsewhere.[14]

The ultraviolet phosphorescence back to the electronic ground state that escapes through a hole in one of the trap electrodes is imaged with a lens onto a photomultiplier tube (PMT). In the upper part of Fig. 2 a semilogarithmic plot of the phosphorescence signal is shown as a function of time. The CO molecules are prepared in the (1,0,1) state at $t=0$ ms, and the strong phosphorescence peak around 4–5 ms results from molecules that pass through the trap with (more or less) the initial beam velocity. At 9.3 ms, the decelerated packet of molecules arrives in the trap center and the trap is switched on. After some initial oscillations, caused by the collective motion of the molecules in the trap, an exponentially decaying phosphorescence signal is observed. This signal is shown on a linear scale in panel (b) of Fig. 2. A weighted least-squares single exponential fit to this data in the time-interval from 13 to 38 ms gives a decay time of 2.63±0.03 ms, where the error is an estimate accounting for the systematic effect of the initial oscillations. The phosphorescence of the trapped molecules is measured in the presence of the trapping fields, i.e., in an electric field ranging from 0 to 10 kV/cm. Under these conditions the opposite parity states of the Λ-doublet are mixed.

For the measurement of the phosphorescence decay of CO molecules in the (2,0,2) level, shown in panel (c) of Fig. 2, the repetition frequency of the molecular beam experiment is reduced from the normally used 10 Hz to 2 Hz to allow for a ~500 ms observation time. To avoid detection of straylight from the excitation laser, that keeps on running at 10 Hz, no phosphorescence signal is recorded during a 6 ms interval around the times that this laser is fired. A single exponential fit to the data in the 50–450 ms interval yields a decay time of 140±4 ms.

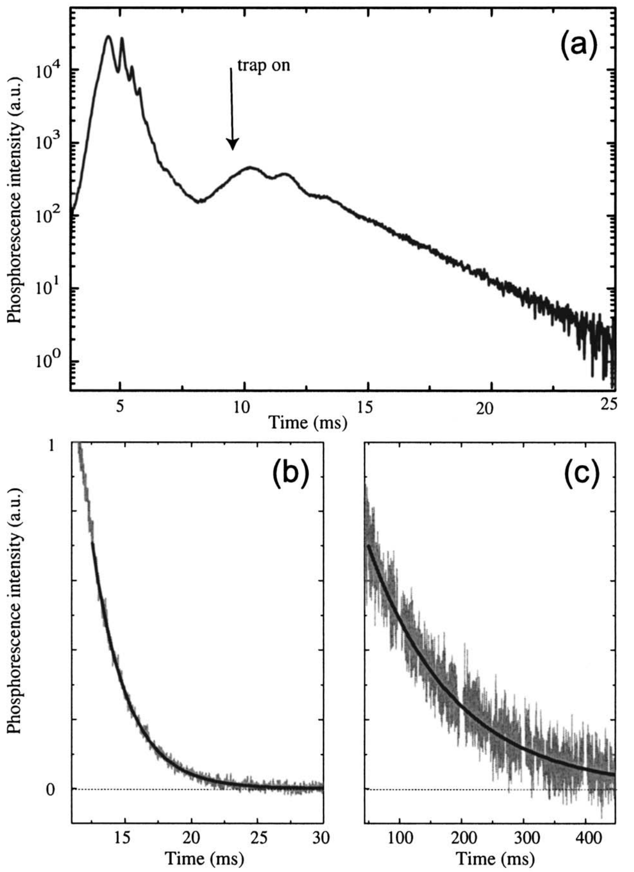

FIG. 2. Semilogarithmic plot of the phosphorescence intensity from the trap region as a function of time after production of CO molecules in the (1,0,1) level in the source chamber (a). The time at which the trap is switched on is indicated by an arrow. Phosphorescence decay curves are shown on a linear scale for CO molecules in the (1,0,1) level (b) and in the (2,0,2) level (c). The solid lines are the results of a weighted least-squares fit to a single exponentially decaying curve.

Apart from the phosphorescence to the ground state, optical pumping by blackbody radiation and collisions with background gas can lead to a decay of the signal of trapped molecules; at the present densities, collisions between trapped molecules do not play a role. Optical pumping due to room temperature blackbody radiation is calculated to proceed at a rate of around 0.014 s^{-1} for CO in the $a\,^3\Pi$, $v=0$ state.[11] The contribution of optical pumping to the overall trap loss rate can therefore safely be neglected. The loss rate due to background collisions was measured to be 0.17 s^{-1} for trapped ground-state OH and OD radicals in this apparatus. As these measurements were done under otherwise identical conditions, we assume the same collisional trap loss rate for metastable CO. For CO molecules in the (1,0,1) level the loss due to collisions can then also be neglected; for molecules in the (2,0,2) level collisions slightly contribute to the observed trap loss rate. After correction for this, a radiative lifetime for CO molecules in the (1,0,1) level of 2.63±0.03 ms is found, whereas the radiative lifetime for molecules in the (2,0,2) level is determined as 143±4 ms. The ratio of these lifetimes is 54.4±1.6, which is in good agreement with the ratio of 54.66±0.01 that is expected from the ratio of the $\Omega=1$ character in the respective wavefunctions.[15]

To calculate the radiative lifetime of the (1,0,1) level, we use the model as originally described by James.[3] Essential in this model are the matrix elements $\langle v_A | h_{A,a}(r) | v_a = 0\rangle$ of the r-dependent spin-orbit coupling $h_{A,a}(r)$ and the matrix elements $\langle v_A | \mu_{A,X}(r) | v_X\rangle$ of the r-dependent electronic $A\,^1\Pi - X\,^1\Sigma^+$ transition dipole moment $\mu_{A,X}(r)$, together with the energy separation of the spin-orbit coupled states. We have computed the wave functions $|v_X\rangle$, $|v_A\rangle$, and $|v_a\rangle$, for the vibrational levels of the $X\,^1\Sigma^+$, the $A\,^1\Pi$, and the $a\,^3\Pi$ states, respectively, with the sinc-function discrete variable representation (DVR) method.[16] The diatomic potentials are computed with the Rydberg-Klein-Rees (RKR) program of Ref. 17, taking the required spectroscopic data for the X-state from Ref. 18 and for the A and a states from Ref. 19.

James approximated the offdiagonal spin-orbit coupling $h_{A,a}(r)$ as minus the diagonal spin-orbit coupling constant of the $a\,^3\Pi$ state, $-h_a(r)$.[3] In the present work we used the full Breit-Pauli spin-orbit operator and we computed the electronic wave functions at the internally contracted multireference single and double excitation (MRCI) level employing molecular orbitals from a state averaged complete active space multiconfigurational self-consistent field (CASSCF) calculation with the MOLPRO computer program. The active space consisted of the full valence space extended with a σ, a π_x, a π_y, and a δ_{xy} orbital (in all calculations C_{2v} point group symmetry was used). The 1s orbitals were optimized but not correlated. The one-electron basis consists of the core-valence correlation consistent quintuple-zeta (cc-pCV5Z) basis set augmented with tight p functions with exponents 462.5 and 950.4 for carbon and oxygen, respectively. The exponents were energy-optimized in atomic calculations. The accuracy of such an approach was demonstrated by Nicklass *et al.*[20] The transition dipole moment $\mu_{A,X}(r)$ was also computed at the CASSCF+MRCI level. The same extended active space was used, but the orbitals for the X and A states were optimized independently and the cc-pV6Z basis was used. The results are presented in Fig. 3.

Using these results, we computed a radiative lifetime for CO molecules in the (1,0,1) state of 3.16 ms. In order to understand the 20% discrepancy with the experimental value, we performed an extensive analysis on the quality of the potentials and on that of the calculations of the spin-orbit coupling and transition dipole moment functions.

James arrived at a calculated value of 2.93 ms for the (1,0,1) level.[3] We repeated the calculation of James by employing RKR potentials based on spectroscopic data available in 1971 and found a value of 2.94 ms. With our new RKR potentials and James' spin-orbit coupling and transition dipole function we obtain 2.93 ms. We therefore do not find the extreme sensitivity to the potential reported by Sykora and Vidal, and cannot reproduce their value of 3.41 ms.[10]

We computed the spin-orbit constants of the vibrational levels in the $a\,^3\Pi$ state, $\langle v_a | h_a(r) | v_a\rangle$, because these can be compared to experimental values. The computed values for the levels $v_a=0-8$ are all between 1.4% and 1.5% lower than the spectroscopic values.[19] We checked the dependence of the spin-orbit coupling on the one-electron basis set by computing $h_{A,a}$ and h_a at $r=2.3a_0$ with a cc-pCVQZ+p and a cc-pCVTZ+p basis set. This gives couplings that are about 0.5% and 1.8% higher, respectively, than the value obtained in the cc-pCV5Z+p basis. We determined the effect of core-valence correlation on the spin-orbit coupling in a calculation with a smaller active space and found that it may increase the couplings by about 0.5%.

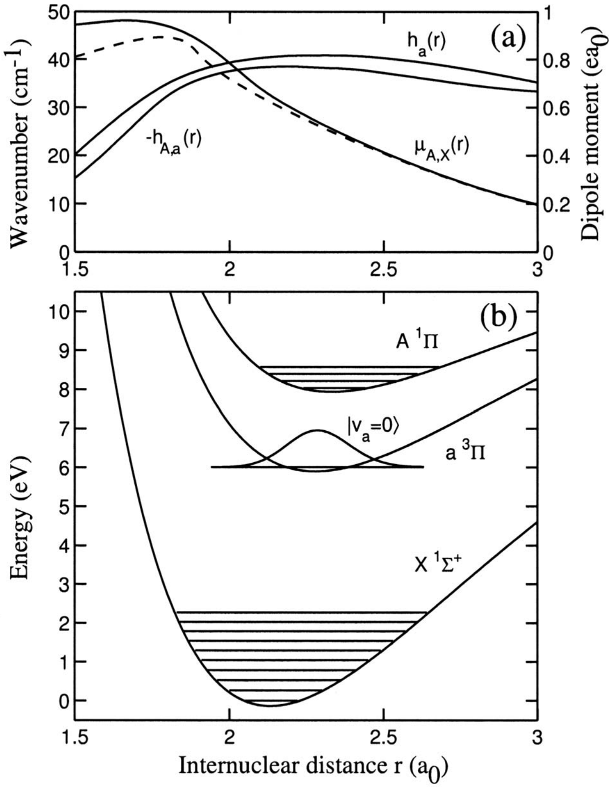

FIG. 3. Panel (a) shows the $A-X$ electronic transition dipole moment $\mu_{A,X}(r)$ (in ea_0) of the present work (the solid line) and from Ref. 21 (the dashed line), together with the diagonal $[h_a(r)]$ and offdiagonal $[h_{A,a}(r)]$ spin-orbit coupling (in cm^{-1}). Panel (b) shows the RKR potentials of the $X\,^1\Sigma^+$, the $a\,^3\Pi$, and the $A\,^1\Pi$ states of CO and the $|v_a=0\rangle$ vibrational wavefunction.

Replacing our $\mu_{A,X}(r)$ with the one computed by Spielfiedel *et al.*[21] gives a value of 3.35 ms for the lifetime of the (1,0,1) level. The *ab initio* method employed in Ref. 21 is similar to ours. The difference between their $\mu_{A,X}(r)$ and ours increases at shorter distances as shown in Fig. 3(a). The main reason for the difference is that we optimize the orbitals for the A and the X states separately, whereas they employed orbitals from a state averaged CASSCF calculation.

We compute a total oscillator strength for the $A\,^1\Pi$, $v \leqslant 12 - X\,^1\Sigma^+$, $v=0$ transitions of 0.1764. This is 2.4% lower than the value of 0.1807 obtained from high resolution electron energy loss spectroscopy.[22] With $\mu_{A,X}$ from Ref. 21 we find a total oscillator strength of 0.1599, i.e., 11.5% below the experimental value.

Another test of $\mu_{A,X}$ is provided by the radiative lifetime measurements of the $A\,^1\Pi$ state by Field *et al.*[23] Their deperturbed values for $v=0-7$ are all of the same quality and decrease smoothly from $\tau(v_A=0)=9.9\pm0.1$ ns to $\tau(v_A=7)=8.95\pm0.1$ ns. In our calculations, however, the lifetimes in-

TABLE I. The $n\,^1\Pi - X\,^1\Sigma^+$ transition dipole moment $\mu_{n,X}$ and the $n\,^1\Pi - a\,^3\Pi$ spin-orbit coupling $h_{n,a}$ at $r=2.3a_0$ computed at the CASSCF+MRCI level (valence CAS extended with two π_x and two π_y orbitals) in an aug-cc-pVTZ basis, the energy separation $n\,^1\Pi - a\,^3\Pi$ (E_n-E_a, with Davidson correction), and the scaled lifetime τ_s of the (1,0,1) level when the states $1,\ldots,n$ are included.

n	E_n-E_a (cm^{-1})	$\mu_{n,X}$ (ea_0)	$h_{n,a}$ (cm^{-1})	τ_s (ms)
1	16 058	0.542	−36.3	3.16
2	48 577	−0.513	0.1	3.15
3	54 284	0.369	−12.9	2.74
4	67 572	0.016	17.7	2.76
5	70 981	0.000	0.2	2.76
6	76 952	0.303	8.9	2.92
7	81 025	−0.105	20.8	2.80

crease from $\tau(0)=8.4$ ns to $\tau(7)=8.6$ ns. Other *ab initio* transition dipole functions, e.g., the one of Ref. 21, also yield lifetimes that increase with v_A. Transition dipole functions fitted to reproduce the measured $A\,^1\Pi$ lifetimes result in computed lifetimes of the (1,0,1) level of 3.5 ms or more.

From the results presented so far, we conclude that a model that takes into account only the $A\,^1\Pi$ intermediate state cannot explain the observed lifetime of the (1,0,1) level. The main sources of error are in the $A-a$ spin-orbit coupling and in the $A-X$ transition dipole moment. It seems unlikely, though, that the combined effect of these errors on the lifetime is more than 10%. Only $^1\Pi$ states can have both a nonzero transition dipole moment to the ground state and a nonzero spin-orbit coupling to the $a\,^3\Pi_1$ state. Therefore, we made an estimate of the contributions of higher lying $^1\Pi$ states by calculating the effective $a-X$ transition dipole moment at $r=2.3a_0$ as a function of the number of intermediate states, using the result to scale the value of 3.16 ms obtained above (Table I). The table shows that the higher states could account for the difference between theory and experiment. We suspect, however, that taking into account their r-dependence and obtaining convergence with respect to the number of $^1\Pi$ states will be difficult.

In this paper, we report the electrostatic trapping of metastable CO molecules. We have exploited the long observation time allowed by the trap to measure the radiative lifetime of two different rotational levels in the $a\,^3\Pi$, $v=0$ state. These two measurements are mutually consistent and yield an accurate value of the radiative lifetime of the $a\,^3\Pi_1$, $v=0$, $J=1$ level of 2.63 ± 0.03 ms. Now that the radiative lifetime of this level is known with unprecedented precision, discrepancies with earlier calculated values have become apparent. This prompted us to perform more detailed calculations for this level. When only spin-orbit coupling of the $a\,^3\Pi$ state with the $A\,^1\Pi$ state is included, we compute a lifetime of 3.16 ms. We show that obtaining agreement between theory and experiment will require the calculation of the contribution of higher $^1\Pi$ states.

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