Population of Long-Lived Vibrational Levels of CO: $I\,^1\Sigma^-$ and $D\,^1\Delta$

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(Received 9 September 1991)

The lowest vibrational energy levels of the $I\,^1\Sigma^-$ and $D\,^1\Delta$ states of CO, which lie approximately 8 eV above the $X\,^1\Sigma^+$ ground state, are predicted to have very long radiative lifetimes, in excess of 1 s for electric dipole transitions. These states cannot predissociate and the couplings with levels of the $A\,^1\Pi$ state are very small. There is, therefore, the possibility of using the $v=0$ levels of the $I\,^1\Sigma^-$ and $D\,^1\Delta$ as reservoirs for highly energetic molecules. In order to encourage experimental studies, methods are proposed for populating the $v=0$ levels of the $I\,^1\Sigma^-$ and $D\,^1\Delta$ states, including stimulated emission from the $W\,^1\Pi$ state.

PACS numbers: 33.70.−w

The phenomenon of metastability, in which an excited state lives orders of magnitude longer than is usual before giving up its energy, is a powerful tool to be used to advantage in the laboratory. Metastable states can be used as "stepping stones" to an energy regime or to entire multiplet systems which are not easily accessible from the ground state. For example, studies of the triplet manifold in H_2 depend critically on the existence of the $c\,^3\Pi_u^-$ metastable state [1–4]. The absence of a single fast decay channel permits the study of competing slower processes such as magnetic dipole and electric quadrupole transitions.

Carbon monoxide is an ideal system in which to explore the phenomenon of metastability, in that it has been extensively studied spectroscopically [5,6] and it has been isolated in inert gas matrices [7]. In a previous paper [8] by Rosenkrantz and Kirby (RK), calculations of the potential energy curves and electron wave functions for the $I\,^1\Sigma^-$ and $D\,^1\Delta$ states of CO were reported. RK computed radiative lifetimes of different vibrational levels, considering vibrational cascade within each electronic state and also decay to the nearby $A\,^1\Pi$ state. In this paper we focus on the $v=0$ levels of the $I\,^1\Sigma^-$ and $D\,^1\Delta$ states, which were shown by RK to have very long radiative lifetimes. We investigate ways of populating these levels, in order to encourage experimental studies of their possible decay mechanisms.

Ab initio potential energy curves [8–10] for low-lying singlet states of CO are illustrated in Fig. 1. It is important to notice that the $A\,^1\Pi$, $I\,^1\Sigma^-$, and $D\,^1\Delta$ states all lie at approximately the same energy (~8 eV) above the $X\,^1\Sigma^+$ ground state and that there are no intervening singlet states. The $I\,^1\Sigma^-$ and $D\,^1\Delta$ states, which both arise from the electronic configuration $\ldots 5\sigma^2 1\pi^3 2\pi$, have very similar potential energy curves and one-electron properties. Electric dipole transitions from the $I\,^1\Sigma^-$ and $D\,^1\Delta$ states to the ground state are forbidden, but these two excited states can, in principle, decay to the $A\,^1\Pi$ state. The close proximity of the $A\,^1\Pi$ state leads to transition probabilities from vibrational levels v' of the $I\,^1\Sigma^-$ and $D\,^1\Delta$ states which range over 5 orders of magnitude, decreasing significantly with decreasing v' [8]. An analogous phenomenon has been noted [11] for the isoelectronic system N_2, in which the $W\,^3\Delta_u$ state lies nearly coincident with the only state to which it can radiate via an allowed electric dipole transition, namely, the $B\,^3\Pi_g$ state.

Although the minimum of the $A\,^1\Pi$ state of CO lies

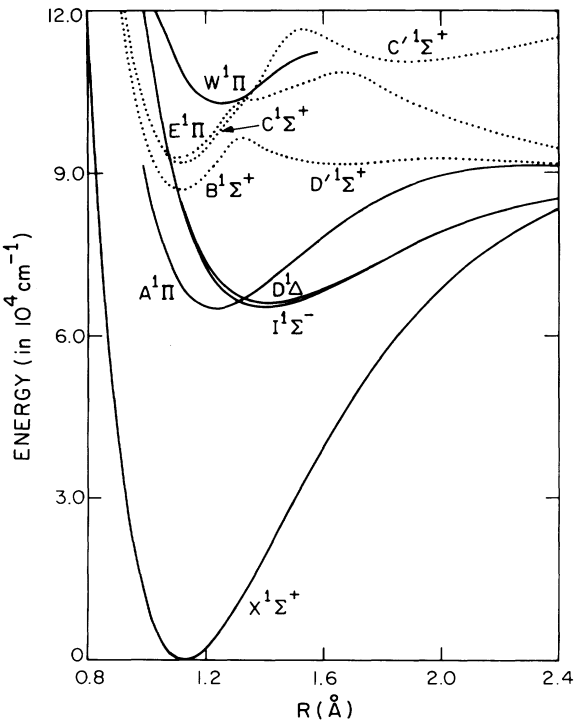

FIG. 1. *Ab initio* potential energy curves for low-lying singlet states of CO.

lower than that of the $I^1\Sigma^-$ state by 8.6 cm^{-1} [12], the difference in the shapes of these two potentials is such that the $I^1\Sigma^-(v=0)$ level actually lies *lower* than $A^1\Pi(v=0)$ by ~ 220 cm^{-1}. The $I^1\Sigma^-(v=0)$ level cannot radiate by an allowed electric dipole transition and will thus be very long lived. The minimum of the $D^1\Delta$ state lies 852.2 cm^{-1} above that of the $A^1\Pi$ state [12]. The $D^1\Delta(v=0)$ level lies ~ 610 cm^{-1} above $A^1\Pi(v=0)$, and this is the one level to which it can radiate by an allowed electric dipole transition. The corresponding lifetime is 1.6 s.

Various vibration-rotation levels of the $I^1\Sigma^-$ and $D^1\Delta$ states have been observed by Simmons, Bass, and Tilford [13] as perturbers of the upper state ($A^1\Pi$) of the fourth positive system. The $v=0$ levels have not been implicated in these perturbations. Also, due to l-uncoupling interactions with certain levels of the $A^1\Pi$ state, it has proved possible to observe very weak absorption from $X^1\Sigma^+(v''=0)$ to certain vibrational levels of the $I^1\Sigma^-$ and $D^1\Delta$ states [14]. The $I^1\Sigma^-(v'=0)$ and $D^1\Delta(v'=0)$ levels have not been observed in this way. The $I^1\Sigma^-$ and $D^1\Delta$ states have also been populated in two-photon transitions from $X^1\Sigma^+(v''=0)$ by Kittrell and co-workers [15]. The only levels observed in this way are $D^1\Delta(v'=7,10,12)$ and $I^1\Sigma^-(v'=7)$.

Experiments on the electron impact excitation of the $I^1\Sigma^-$ and $D^1\Delta$ states [16,17] do not yet have vibrational resolution, but it seems clear from appearance potentials of 9.5 to 10.0 eV, and the measured lifetimes $\tau \sim 80$ μs or $\tau \sim 97$ μs, that both sets of experiments are consistent with the population of levels with $v \geq 10$.

In spite of the range of observations of the $D^1\Delta$ and $I^1\Sigma^-$ states of CO, there is no evidence that the $v=0$ levels of either of these states has ever been observed. The fundamental problem with populating the $v'=0$ levels of the $I^1\Sigma^-$ and $D^1\Delta$ states from $X^1\Sigma^+(v''=0)$ either by two-photon absorption or by electron impact excitation is that the Franck-Condon overlaps for such a transition are vanishingly small. The Franck-Condon overlaps of the $v'=0$ and $v'=1$ levels of the $I^1\Sigma^-$ state are shown in Fig. 2 as functions of v'' for the $X^1\Sigma^+$ state. The corresponding figure for the $D^1\Delta$ state is very similar, and thus is not shown. The strongest transitions populating the $v'=0$ levels, with $|\text{overlap}|^2$ greater than 0.1, originate from ground-state levels with $v''=8$ to 12. Vibrationally excited levels of the $X^1\Sigma^+$ state have been used before in absorption spectroscopy; see, for example, studies of the $B^1\Sigma^+ \leftarrow X^1\Sigma^+$ transition by Wolk and Rich [18] and of $A^1\Pi \leftarrow X^1\Sigma^+$ by DeLeon [19].

Another possible means of populating the $v=0$ levels of the $I^1\Sigma^-$ and $D^1\Delta$ states is by cascade from higher-lying vibrational levels of these states. However, this cascade is predicted to be much less probable than radiative decay to the $A^1\Pi$ state [8]. The one exception is the $v=1$ level of the $I^1\Sigma^-$ state which preferentially (by a factor of 2) radiates to $I^1\Sigma^-(v=0)$. Another plausible mechanism

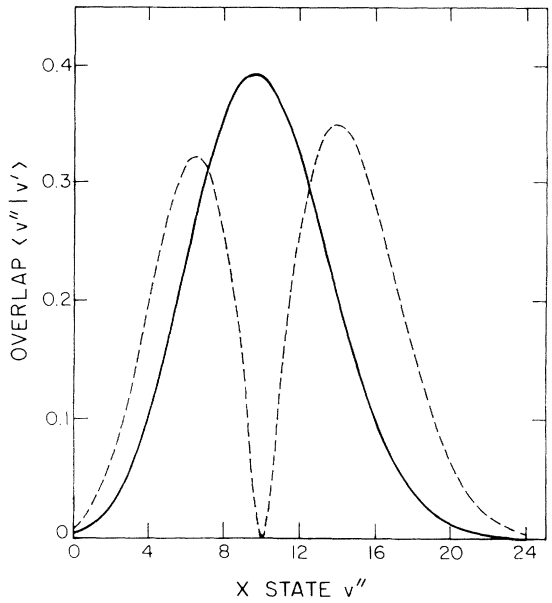

FIG. 2. Franck-Condon overlaps of the $v'=0$ (——) and $v'=1$ (---) levels of the $I^1\Sigma^-$ state with levels v'' of the $X^1\Sigma^+$ state.

for populating these elusive levels is charge transfer from CO^+. Indeed, the most effective mechanism for populating the important $c^3\Pi_u^-$ state of H_2 is charge transfer collisions of H_2^+ in cesium vapor [4].

An interesting alternative mechanism for populating $I^1\Sigma^-(v=0)$ and $D^1\Delta(v=0)$ involves emission from the higher-lying $W^1\Pi$ state. Transitions involving the $W^1\Pi$ state have been observed by Ogawa and Ogawa [20] by Tilford and Simmons [21], and by Sekine, Adachi, and Hirose [22]. This state is the first member of a Rydberg series converging to the $A^2\Pi$ excited state of CO^+. Cooper and Kirby [10] have carried out an *ab initio* study of this state, including a calculation of the $W^1\Pi$-$X^1\Sigma^+$ oscillator strength, which confirmed the very strong nature of this transition.

Using wave functions presented previously [8–10], we have now calculated transition probabilities for the decay of various vibrational levels of the $W^1\Pi$ state to seven lower-lying singlet electronic states. The results are summarized in Table I. Null entries in the table denote transition probabilities which are estimated to be less than 0.05×10^7 s^{-1}. Most of the radiative decay from the $W^1\Pi$ state takes place to the $X^1\Sigma^+$ state. The $W^1\Pi$-$C^1\Sigma^+$ and $W^1\Pi$-$E^1\Pi$ transition probabilities are particularly small because of the small v^3 factors for these transitions. Transition probabilities to the $D'^1\Sigma^+$ state are negligible. Our calculations are consistent with the observation of Sekine, Adachi, and Hirose [22] that the $W^1\Pi(v'=0)$-$B^1\Sigma^+(v''=0)$ transition is weak. We calculate a transition probability for this transition of 0.03 $\times10^7$ s^{-1}.

TABLE I. Transition probabilities $A_{v'}$ (in $10^7\ s^{-1}$) for vibrational levels of the $W^1\Pi$ state decaying via allowed electric dipole transitions to lower-lying electronic states. A null entry indicates a value not greater than $0.05\times10^7\ s^{-1}$.

v'	$X^1\Sigma^+$	$B^1\Sigma^+$	$C^1\Sigma^+$	$A^1\Pi$	$E^1\Pi$	$I^1\Sigma^-$	$D^1\Delta$
0	23.8	···	···	0.1	···	0.5	0.8
1	23.2	0.1	···	0.2	···	0.5	0.7
2	26.7	···	···	0.1	···	0.5	0.7
3	29.3	···	···	0.1	···	0.5	0.7
4	28.9	0.1	···	0.1	···	0.5	0.7

TABLE II. Transition probabilities $A_{v''v'}$ (in $10^7\ s^{-1}$) from given vibrational levels v' of the $W^1\Pi$ state to vibrational levels v'' of the $I^1\Sigma^-$ and $D^1\Delta$ states.

	$I^1\Sigma^-$		$D^1\Delta$	
v'	$A_{0v'}$	$\sum_{v''\neq0}A_{v''v'}$	$A_{0v'}$	$\sum_{v''\neq0}A_{v''v'}$
0	0.03	0.47	0.04	0.71
1	0.11	0.41	0.12	0.62
2	0.16	0.36	0.19	0.55
3	0.14	0.36	0.20	0.73
4	0.08	0.40	0.14	0.72

We predict the largest $W^1\Pi(v')$-$X^1\Sigma^+(v''=0)$ oscillator strength to be for $v'=2$. However, no emission has ever been observed for vibrational levels of the $W^1\Pi$ state with $v'\geq1$ and it appears that strong predissociation eradicates all but the lowest vibrational level.

The transition probabilities from the $W^1\Pi(v'=0)$ state are shown in Fig. 3 as functions of v'' for the $I^1\Sigma^-$ and $D^1\Delta$ states. For $W^1\Pi(v'=0)$ we predict branching ratios for radiative decay to the $I^1\Sigma^-$ and $D^1\Delta$ states of 2% and 3%, respectively. Branching ratios for radiative decay to the $v''=0$ levels of the $I^1\Sigma^-$ and $D^1\Delta$ states are approximately 0.15% in each case. Transition probabilities to $v''=0$ and to $v''\neq0$ are collected in Table II. These branching ratios could be made considerably more favorable by the process of stimulated emission from $W^1\Pi(v'=0)$, in which a laser of suitable frequency is used to populate preferentially $I^1\Sigma^-(v''=0)$ or $D^1\Delta(v''=0)$.

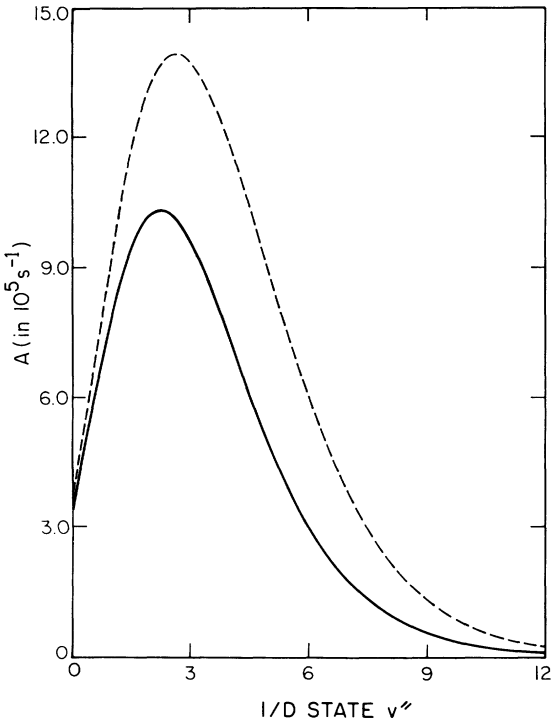

FIG. 3. Transition probabilities $A_{v''}$ for electric dipole transitions from $W^1\Pi(v'=0)$ to levels v'' of the $I^1\Sigma^-$ (——) and $D^1\Delta$ (---) states.

Finally, having suggested methods for producing these elusive vibrational levels, we speculate very briefly on possible decay mechanisms. Both the $I^1\Sigma^-$ and $D^1\Delta$ states have allowed magnetic dipole and electric quadrupole transitions to lower-lying states. Electric quadrupole transitions from $I^1\Sigma^-$ and $D^1\Delta$ to the $X^1\Sigma^+$ state appear to have lifetimes on the order of $\tau\sim0.1$ s, assuming ΔE values on the order of 6 eV. An identification of an electric quadrupole transition of this molecule would be noteworthy, as such transitions do not appear to have been observed for heteronuclear diatomics.

In addition, there is the possibility of intensity stealing from allowed electric dipole transitions. As mentioned previously this has allowed for observation of very weak absorption in $X^1\Sigma^+$-$D^1\Delta$ and $X^1\Sigma^+$-$I^1\Sigma^-$ for particular vibration-rotation transitions—but not involving the $v'=0$ levels. The $I^1\Sigma^-$ and $D^1\Delta$ potential curves lie nested within the $e^3\Sigma^-$, $d^3\Delta$, and $a'^3\Sigma^+$ potential curves but significant spin-orbit interaction with these states is not expected. The only spin-orbit interaction worth noting for both metastable states may be with the $a^3\Pi$ state, the upper state of the much-studied Cameron bands. The $v=0$ levels of the $I^1\Sigma^-$ and $D^1\Delta$ states are located near $v=10$ and 11 of the $a^3\Pi$ state, and so any perturbations are likely to be strongly j dependent. The $a^3\Pi$ state is itself metastable with lifetimes for decay ($a^3\Pi$-$X^1\Sigma^+$) on the order of 10 ms, so that even if the spin-orbit mixing is large, there will not be rapid loss through this channel.

Of our various proposals for generating the long-lived $v'=0$ levels of the $I^1\Sigma^-$ and $D^1\Delta$ states, the most interesting one, and potentially the most useful, is stimulated emission from the $W^1\Pi$ state. It is worth recalling that this Rydberg state is connected via a very strong transition ($f_{00}=0.005$) to the $v''=0$ level of the $X^1\Sigma^+$ ground state.

This research was supported by a grant from the Air Force Office of Scientific Research No. AFOSR-88-0042.

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