Photochemically Induced Electronic-To-Electronic Energy Transfer in Geminate CO···O van der Waals Pair Generated through Vacuum Ultraviolet Photolysis of CO_2 in Ar Matrices

Murthy S. Gudipati[†]

Institut für Physikalische Chemie, Universität zu Köln, Luxemburger Strasse 116, D-50939 Köln, Germany

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An intracage geminate CO···O van der Waals pair is generated through vacuum ultraviolet (VUV) photolysis of 0.1% CO_2 in Ar matrices at 18 K. Excitation of CO between 157 and 130 nm ($A^1\Pi \leftarrow X^1\Sigma^+$ vibronic transitions) results in a strong emission due to the $^1S \rightarrow {}^1D$ transition of O at 560 nm and weak emission bands due to CO and O_2. The band at 560 nm is absent in the emission spectra measured from CO in Ar (1:1000) or O_2 and CO in Ar (1:1:1000) matrices. The observed phenomenon is due to *photochemically induced electronic-to-electronic energy transfer*. Excited CO and ground-state $O(^3P)$ undergo chemical recombination to result in excited CO_2, which dissociates to ground-state CO ($X^1\Sigma^+$) and excited $O(^1S)$. Other possible pathways are also discussed but shown to be inappropriate.

Introduction

Electronic energy transfer (EET) is one of the most important aspects of photophysics and photochemistry.[1−6] Photoinduced EET processes ($D^* + A \rightarrow D + A^*$) are normally divided into two categories, namely, resonant and nonresonant. Resonant EET occurs when the excitation energy of the acceptor (A) is close to the energy of one of the excited states of the donor (D), namely, $\Delta E = (E_{D^*} - E_{A^*}) \cong 0$. This kind of EET, which is commonly observed, is governed by the long-range dipole−dipole interactions or short-range exchange interactions, also known as Förster−Dexter mechanism[1,2] in organic photophysics.[7] Under nonresonant conditions, in addition to photophysical EET processes[8] where excess energy of D is dissipated into the surrounding "bath" vibrations in condensed media, EET can also occur through the formation of a chemically bound excited $(DA)^*$ species,[5,9] which later dissociates to $D + A^*$. Such a *photochemically induced excitation energy-transfer* process, where spectroscopic observation of A* is thought to be less common,[6] is dealt with in the present publication by combining the experimental results with already known theoretical data on CO_2, CO, and O. Since the early days of photoinduced EET (known as *sensitization*[10]), most EET processes that did not follow any resonant criteria were thought to involve an excited $(DA)^*$ species.[9] Such a mechanism, namely, $D^* + A \rightarrow (DA)^* \rightarrow D + A^*$, has strongly been advocated by Schenck[5,11] to explain "*sensitized photochemistry*" of organic molecules. Historically, it seems that Mrozowski[12] was one of the first to propose[5] the involvement of such a $(DA)^*$ complex in order to explain sensitized luminescence in Hg + Tl gas mixtures.

In the course of time, photoinduced EET has become an important aspect of photophysics[4,13−15] and photochemistry.[16−18] EET processes are observed in the gas phase,[9,19] in the fluid-phase,[6] in molecular crystals,[20] in liquid crystals,[21] and more recently, in low-temperature matrices.[22−24] These processes involve electronic (E), vibrational (V), and rotational (R) EET, namely, E → E, E → V, V → E, and V → R. To the best of our knowledge there has been no systematic spectroscopic study that deals with *photochemically induced* E → E EET, which will be presented here.

Photophysical and photochemical properties of CO_2 are important for understanding atmospheric photochemistry not only of our planet but also of other planets such as Mars and Venus.[25] Extensive experimental[26] and theoretical[27] work has been published on the electronic spectra and dissociation dynamics[28] of CO_2 as well as energy transfer from excited O atoms to CO in the gas phase.[29,30] However, relatively little is known about the spectroscopy and photochemical behavior of CO_2 in condensed media, especially in rare-gas matrices. These investigations[31] (except one[32] that deals with excitation spectra of CO_2), however, deal with the generation and mobility of O atoms using CO_2 as a precursor. Taylor et al.[32] have measured excitation spectra of 1% CO_2 in an Ar matrix between 10 and 12 eV by monitoring the $^1S \rightarrow {}^1D$ (from now on SD) emission of O. Around the same time Fournier et al.[31] have shown that photolysis of 0.1% CO_2 in Ar matrices at 147 nm results in the SD emission of O at 561.5 nm. Recently, we reported[33] the excitation spectra of O atoms that are generated through photolysis of 1% O_2 as well as 1% N_2O in Ar matrices. We have shown that excitation of stable $O(^3P)$ in matrices causes the SD emission of O, contrary to what was believed before[31] that this emission occurs only during the photolysis of a precursor molecule generating excited $O(^1D)$, which by absorbing a second photon reaches the $O(^1S)$ state.

In this article we present excitation spectra that are measured monitoring the SD emission of O from 0.1% CO_2 in Ar matrices. It will be shown that an intracage geminate pair of CO and O is formed. A cyclic process of excitation of CO, $CO^* + O(^3P)$ recombination to CO_2^*, dissociation of CO_2^* to $CO(X^1\Sigma^+)$ and $O(^1S)$, and finally the SD emission of O, is the mechanism that explains the observed spectra. Such a mechanism is also consistent with the theoretical data available on the electronically excited states of CO_2 correlated to those of CO and O.[27] This very mechanism could also explain why Fournier et al.[31] observed the SD emission of O by exciting CO_2 in Ar matrices at 147 nm, where CO itself absorbs.

Experimental Section

The experiments were carried out at the Berlin Synchrotron Radiation Facility (BESSY) using a 3 m normal incidence monochromator (3m-NIM-1) equipped with an Al grating (600 lines/mm). All the experimental details are given in an earlier

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[†] Fax: +49-221-470-5144. E-mail: murthy@hartree.pc.uni-koeln.de.

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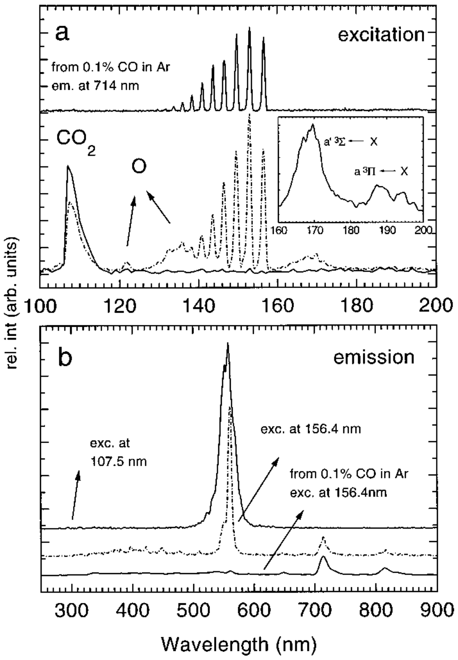

Figure 1. (a) Excitation spectra measured by monitoring the SD emission of O at 558 nm before (solid) and after (dashed) photolysis of 1% CO_2 in an Ar matrix. Insert on the right side shows the excitation spectrum between 160 and 200 nm that corresponds to singlet−triplet excitations in CO. For comparison an excitation spectrum of 0.1% CO in Ar matrices is shown on the top. (b) Emission spectra measured by exciting 0.1% CO_2 in Ar matrices at 107.5 nm (solid) that results in dissociative excitation of CO_2 and 156.4 nm (dashed) that corresponds to A(0) ← X(0) excitation of CO. In both cases strong emission from O due to the SD transition is observed. For comparison an emission spectrum measured from 0.1% CO in an Ar matrix by exciting at 156.4 nm is also shown.

publication.[33] High-purity Ar(99.999%) and O_2(99.995%) from Linde and CO and CO_2, both (99.995%) from Messer-Griesheim, were used to generate optically clear matrices on a LiF window at 18 K. After deposition the cryostat was rotated so that the matrices face the incoming synchrotron beam in order to avoid transmission cutoff due to the LiF window. The measured spectra were corrected for changes in the current of the storage ring but not for the monochromator functions.

Results

Excitation spectra measured at 1 nm intervals from a freshly prepared 0.1% CO_2 in an Ar matrix, as well as after about an hour of photolysis, are shown in Figure 1a. The emission was monitored at 558 nm. Photolysis was carried out by means of measuring several excitation spectra of CO_2 between 100 and 200 nm, amounting to about 3000 s photolysis time. Afterward, no significant change in the intensities of excitation bands of CO_2 or CO has been noticed. It can be seen from the intensities of the band centered at 107.5 nm that about 25% CO_2 has been photolyzed during this period. After the photolysis, excitation bands due to CO (157−130 nm) and due to O (133 and 121 nm) can clearly be identified. Excitation spectra of CO in rare-gas matrices are thoroughly investigated by Schwentner and co-workers,[34,35] which will be referred to at a later point in this article. Excitation bands at 130 and 121 nm due to O in Ar matrices were identified by us in our earlier investigations.[33] For comparison, an excitation spectrum measured by monitoring the emission band at 714 nm of 0.1% CO in an Ar matrix is also included in this figure.

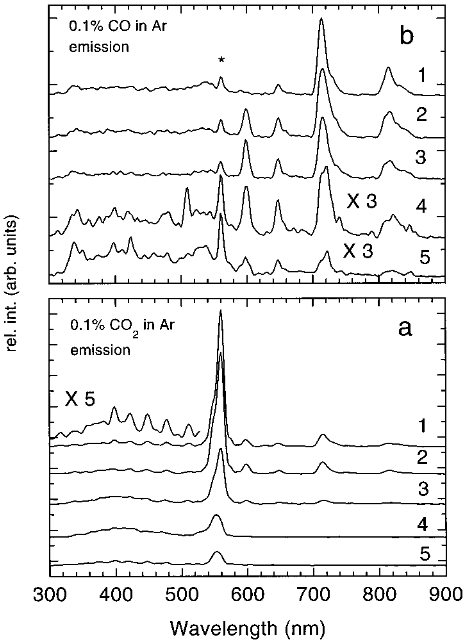

Figure 2. (a) Emission spectra measured while exciting at different wavelengths that correspond to A(v') ← X(0) transitions in CO (1, $v' = 1$; 2, $v' = 2$; 3, $v' = 4$; 4, off resonance at 170 nm; 5, off resonance at 150.7 nm) from 0.1% CO_2 in an Ar matrix after photolysis. SD emission due to O atom at 560 nm is more than an order of magnitude intense compared to the strongest emission from CO itself at 714 nm. (b) Emission spectra recorded by exciting 0.1% CO in an Ar matrix at different wavelengths that correspond to A(v') ← X(0) transitions in CO (1, $v' = 0$; 2, $v' = 1$; 3, $v' = 2$; 4, $v' = 4$; 5, $v' = 6$). The asterisk is labeled at 560 nm emission that is due to traces of photolyzed CO_2 impurity in the matrix.

Emission spectra measured between 250 and 900 nm in 2 nm intervals while exciting Ar matrices containing 0.1% CO_2 at 107.5 and 156.4 nm are shown in Figure 1b. An emission spectrum obtained by exciting 0.1% CO in Ar matrices at 156.4 nm is also included for comparison. Excitation of CO_2 at 107.5 nm results in only one broad emission band between 500 and 600 nm with a maximum at 558 nm, whereas a narrow band between 540 and 580 nm with a maximum at 560 nm, several weak bands between 350 and 540 nm, and two bands at 714 and 816 nm, respectively, are measured by exciting these matrices at 156.4 nm after the photolysis of CO_2. It is important to note that the emission band at 560 nm is absent in the spectrum of 0.1% CO in Ar matrices recorded during excitation at 156.4 nm, which corresponds to the 0−0 of $A^1\Pi \leftarrow X^1\Sigma^+$ transition in CO.

The results presented in Figure 1 indicate that an energy transfer occurs between the excited CO molecule and the O atom. It has been established from our earlier investigations[33] that the SD emission can only occur when O atoms are excited at wavelengths shorter than 147 nm in Ar matrices. To gain more experimental evidence that indeed CO is excited at 156.4 nm that results in SD emission of O, a series of emission spectra have been recorded by tuning the synchrotron light to each of the $A^1\Pi \leftarrow X^1\Sigma^+$ vibronic transitions in CO. Some of these spectra are collected in Figure 2a. In addition, emission spectra were also measured by exciting the matrices where CO shows a minimum between two bands (off resonance at 150.7 nm) as well as at 170 nm where a broad excitation band is observed (Figure 1a insert). The corresponding emission spectra measured from 0.1% CO in Ar are shown in Figure 2b. A comparison between parts a and b of Figure 2 reveals that both the SD emission band at 560 nm as well as several weak bands between 300 and 500 nm (due to A′ → X emission in O_2) are absent in Figure 2b. After the photolysis of CO_2, excitation spectra have been measured by monitoring emission at 560, 598,

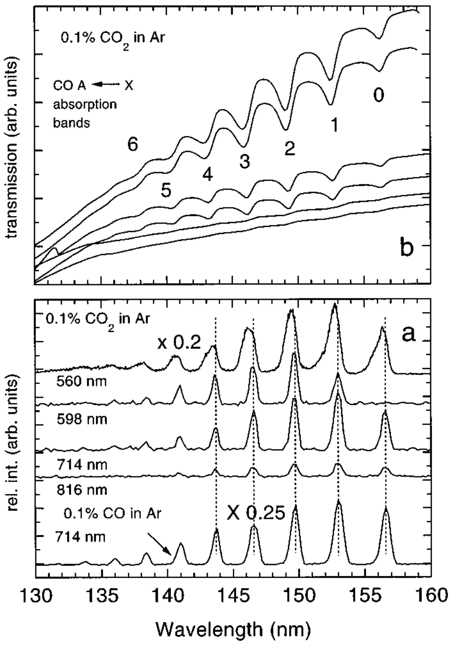

Figure 3. (a): Excitation spectra measured at 0.1 nm intervals from photolyzed 0.1% CO_2 in an Ar matrix. Emission was monitored at different wavelengths as shown. For comparison an excitation spectrum measured from 0.1% CO in an Ar matrix is also shown at the bottom. Vertical dashed lines are drawn to guide the eye to differentiate between excitation spectra of perturbed (by the presence of O in the same matrix cage) and unperturbed CO. (b) Transmission spectra measured during the photolysis of 0.1% CO_2 in Ar. The bottom curve is from a freshly made matrix. The top curve is measured after equilibrium has been reached at about 3000 s. No significant growth of the CO absorption bands has been found with prolonged photolysis.

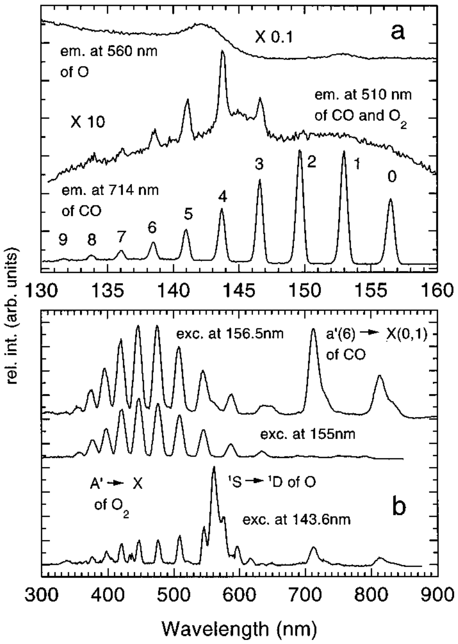

Figure 4. (a) Excitation spectra measured from a O_2:CO:Ar = 1:1:1000 matrix. The bottom curve shows A ← X transitions in CO. The middle curve shows A ← X transitions in CO and the B ← X transition (Schumann-Runge Continuum) in O_2. The top curve shows the excitation spectrum of the O atom in an Ar lattice. (b) Emission spectra measured from the same matrix. The band progression centered at 450 nm is due to A′ → X transitions in O_2 (Herzberg III system). Two broad bands at 714 and 816 nm are due to a′(6) → a(0,1) transitions in CO. Emission at 560 nm is due to $^1S \rightarrow {}^1D$ transition in O atoms in an Ar lattice.

714, and 816 nm. These spectra are shown in Figure 3a along with the excitation spectrum measured from 0.1% CO in Ar matrices by monitoring the emission at 714 nm. Thus, obtained excitation bands of CO (a photoproduct of CO_2 in Ar matrices) are much broader when SD emission of O at 560 nm was monitored compared to those measured by monitoring the hot emission of CO itself at 598, 714, and 816 nm. Excitation spectra recorded by monitoring the hot emission of CO (a photoproduct of CO_2 in Ar matrices) are identical with the spectrum measured from CO itself in Ar matrices, indicating that the hot emission bands of CO arise only from an unperturbed and isolated CO. The SD emission of O at 560 nm occurs only when CO is strongly perturbed by its surroundings in Ar matrices.

Transmission spectra have been measured simultaneously during the measurements of excitation spectra using a GaAs photodiode. A selected set of these spectra are shown in Figure 3b. The bottom curve was recorded from a freshly deposited 0.1% CO_2 in an Ar matrix, which shows a negligible amount of CO absorption. Upon further irradiation the absorption bands of CO grew steadily. These spectra further confirm that CO is generated only during the photolysis but not present as an impurity in the matrices.

Thus, the experimental information obtained so far clearly reveals that CO and O that are generated during the photolysis of CO_2 in Ar matrices participate in the energy-transfer process. However, we still do not know whether CO and O are far removed from each other, as in the case of V−E energy transfer between CO and O_2 in rare-gas matrices discovered by Dubost and co-workers,[24a,c] or close to each other. Bahrdt and Schwentner reported[34a] that they did not observe E−E energy transfer between 210 and 175 nm excitation from an O_2:CO:Ar (1:10:1000) matrix. Our experiments conducted on O_2:CO:Ar (1:1:1000) confirm these results in the wavelength region between 200 and 100 nm. We have also found that no E−E energy transfer occurs between CO and O that is generated through photolysis of O_2. These results summarized in Figure 4 are discussed in detail in the next section. In summary, energy transfer is not detected when O atoms are produced from a different precursor (here O_2), which does not lead to close proximity of CO and O.

Discussion

CO_2. The strongest absorption bands of CO_2 in the gas phase are located between 120 and 106 nm.[26] This part of the spectrum is highly congested with irregularly spaced absorption peaks. Starting with a band at 113 nm, the region between 113 and 106 nm has been assigned to excitation into the Rydberg states, namely, the $^1\Sigma_u^+$, $^3\Sigma_u^-$, $^3\Pi_u$, and $^1\Pi_u$ states.[26d] The region between 120 and 114 nm consists of a quasi-regularly spaced band progression. A detailed interpretation of the gas-phase spectra of CO in this region can be found in the literature.[26d,e] Cossart-Magos et al.[26d] proposed that the terminating state that is responsible for the band progression between 120 and 114 nm is a valence state with the same symmetry as the strongly allowed Rydberg state, namely, $^1\Sigma_u^+$. This valence state correlates to O(^{1}S) and CO($X^1\Sigma^+$) after dissociation.[27a] Cossart-Magos et al.[26d] further proposed that the valence state $^1\Sigma_u^+$ is dissociative along the asymmetric stretch coordinate and bound along the symmetric stretch and bending coordinates and that the valence state efficiently predissociates the Rydberg state $^1\Sigma_u^+$.

Under matrix conditions, so far the only available excitation spectrum was reported by Taylor et al.[32] They have also observed a progression of about 687 cm^{-1} superposed on a broad continuum. However, this progression starts only at about 113

TABLE 1: Wavelengths (in nm) of the Excitation Bands Due to A(v') ← X(v'' = 0) Transitions and Emission Bands Due to e → a, d → a, and a′ → a Transitions in CO Isolated in Ar Matrices

A(v') ← X(v'' = 0) Excitation Bands

v′	0	1	2	3	4	5	6	7	8	9
present work	156.6	153.0	149.7	146.6	143.6	141.0	138.4	136.0	133.8	131.7
Bahrdt[a]	156.4	152.7	149.5	146.4	143.4	140.7	138.3	135.8	133.6	131.4

Emission Due to the $a^3\Pi(v'')$ Final State

	e(8) → a(0)	e(4) → a(0)	d(4) → a(0)	d(3) → a(0) or e(0) → a(0)	a′(6) → a(0)	a′(6) → a(1)
present work	424.0	510.0	599.0	648	714	816
Bahrdt[a]	425.6	510.7	598.7			

[a] Reference 35.

nm and spans down to 108 nm. These bands can neither be correlated to the Rydberg nor to the valence states in the gas phase. If they are due to the Rydberg transitions, then the expected blue shift of Rydberg transitions in matrices[36] is not observed. If these bands are due to excitation into the bound surface of the valence $^1\Sigma_u^+$ state, then the blue shift from 118.4 nm to about 113 nm is unexplainable. Our excitation spectrum differs from that of Taylor et al. We observe unresolved bands as also found by Taylor et al., but the vibrational spacing of ~1200 cm^{-1} is significantly different from 687 cm^{-1} reported by them. Interpretation of the spectra of CO_2 is further complicated by the excitation bands between 117 and 100 nm of the photoproduct CO due to B ← X, C ← X, and E ← X transitions.[34d] Further experimental and theoretical investigations on CO_2 and its isotopomers are necessary in order to clarify these differences and get more information on the spectroscopic properties of CO_2 in matrices.

CO. Schwentner and co-workers[34,35] thoroughly investigated the spectroscopic properties of CO in rare-gas matrices. However, the $A^1\Pi \leftarrow X^1\Sigma^+$ transition of CO only in Ne matrices has been published by these authors.[34c] The data pertinent to other matrices (Ar and Kr) can be found in the doctoral thesis of Bahrdt.[35] In the present study more emission bands could be observed in the near-infrared region, which lie beyond the detection limit of the photomultiplier employed by Bahrdt and Schwentner. The spectroscopic data from the present investigation, collected in Table 1, are in good agreement with the data of Bahrdt.[35] The band at 648 nm (Figure 2) could be due to the $e^3\Sigma^-(v' = 0) \rightarrow a^3\Pi(v'' = 0)$ or $d^3\Delta(v' = 3) \rightarrow a^3\Pi(v'' = 0)$ transitions (Figure 5). The corresponding emission from the final e state to the ground state has been observed by Bahrdt.[35] The energy of 1750 cm^{-1}, the difference between the 714 and 816 nm bands, clearly corresponds to the difference between $v' = 0$ and $v' = 1$ of the a state. Hence, these bands should result from the same final state, and we identify this state as $a'^3\Sigma^+(v' = 6)$. These bands, blue-shifted by ~6 nm from the gas-phase values, belong to the Asundi emission band system.[37] Beyond the 816 nm band, so far no emission from CO in rare-gas matrices is reported in the near-infrared region. From the same final state, namely, the $a'^3\Sigma^+(v' = 6)$ state, emission to the ground state has also been observed by Bahrdt.[35]

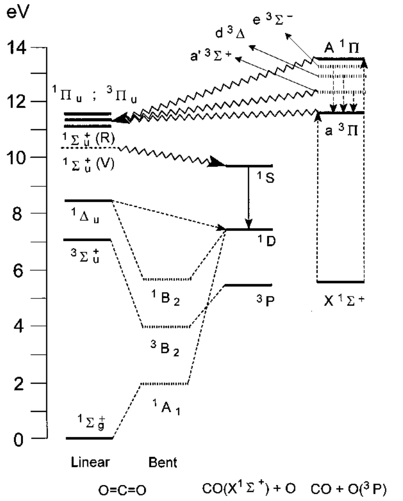

Figure 5. Schematic representation of the photochemically induced electronic-to-electronic energy transfer observed from intracage geminate CO···O pair in Ar matrices. Energies of various electronic states of CO_2 are taken from refs 27 and 30. Relevant electronic states of CO_2 both as a linear and a bent molecule are given on the left side. R and V denote Rydberg and valence states, respectively. Electronic states of CO and O at the van der Waals separation are shown on the right side. Dotted vertical lines with arrowheads pointing upward show excitation in CO, and the solid vertical line with an arrowhead pointing downward represents the emission in an O atom. Slanted zigzag lines follow the energy-transfer process. Dotted vertical lines with arrowheads pointing downward represent triplet−triplet emission from isolated CO molecules.

O_2 and CO. The results pertinent to the present study are summarized in Figure 4. These spectra were measured from Ar matrices containing 0.1% CO and 0.1% O_2. Spectroscopic properties of O_2 in rare-gas matrices at longer wavelengths than 200 nm are well studied.[38] The strongest absorption of O_2 in the gas phase occurs between 205 and 135 nm through the $B^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ transition. The Schumann−Runge bands that result from excitation into the bound region of the B ← X transition have recently been reinvestigated in rare-gas matrices.[39] At wavelengths shorter than 170 nm, excitation spectra of O_2 in rare-gas matrices[33,40] still need interpretation.[41] Excitation of O_2 at wavelengths between 205 and 100 nm results in strong emission bands, known as Herzberg III bands, due to the $A'^3\Delta_u(v' = 0, \Omega = 3) \rightarrow X^3\Sigma_g^-$ transition[38] between 300 and 700 nm (Figure 4). The corresponding excitation spectrum, by monitoring any of the A′ → X bands, is a continuum between 180 and 100 nm with a dip around 121 nm.[33,41] After dissociative excitation of O_2, a major portion of the O atoms undergo intracage geminate recombination and subsequently relaxes to the X state through radiative and nonradiative processes. However, a small number of the O atoms escape the mother cage. Excitation spectra of O atoms that are generated through photolysis of O_2 or N_2O in Ar matrices are active only at wavelengths shorter than 147 nm (Figure 4a).[33] It is of importance here to note that if O atoms do not interact with CO, then we should observe the SD emission of O only when excited at wavelengths shorter than 147 nm.

Excitation and emission spectra shown in Figure 4 clearly reveal that the energy transfer between CO and O (which is generated by the photolysis of O_2) does not occur. Owing to high dilution, it is extremely unlikely that O_2 and CO are close to each other in the matrices. When excited at 156.4 nm, corresponding to the $A(v' = 0) \leftarrow X(v'' = 0)$ transition of CO or the B ← X continuum of O_2, only the Herzberg III bands of O_2 and the emission at 648, 714, and 816 nm from CO could be observed. Contrary to the results from CO_2 in Ar matrices, the SD emission of O is now completely absent when excited at 156.4 nm, though O atoms are present in the matrix. Excitation at 155 nm, where neither CO (Figure 4a) nor O absorbs, results only in the $A' \rightarrow X$ emission bands of O_2. On the other hand, for excitation at 143.6 nm that corresponds to the $A(v' = 4) \leftarrow X(v'' = 0)$ transition in CO, where O_2 as well as O also absorb, emission from all of the three species can be detected (Figure 4b). The excitation spectrum (Figure 4a) measured by monitoring the emission at 714 nm is identical with the corresponding spectrum shown in Figure 3a, indicating that in both the cases, the spectra result from isolated CO. At 510 nm both CO and O_2 show emission. Observation of the excitation bands of CO with $v' > 3$ by monitoring the 510 nm emission is consistent with the observations of Bahrdt and Schwentner.[34c] From these results we can confidently conclude that in matrices containing CO and O_2 at high dilution, no energy transfer of any kind takes place when excited between 200 and 100 nm. Thus, these experiments on CO_2, CO, and O_2 in Ar matrices reveal that it is absolutely necessary for CO and O to be in very close proximity in order to observe the energy transfer.

Energy Transfer from CO to O. The experimental data obtained from (a) 0.1% CO_2, (b) 0.1% CO, and (c) 0.1% O_2 and 1% CO in Ar matrices, which is presented in this article, shows that the energy transfer from CO to O occurs only when CO_2 is photolyzed. Absence of this process in matrices with O_2 and CO indicates that proximity of CO and O is necessary for energy transfer to take place. The question is whether it is also necessary for CO and O to coexist in the same matrix cavity or whether CO and O can occupy, at the minimum, adjacent cavities. In the following we consider the various possible EET processes that could take place under the given experimental conditions. The experimental data presented here will then be compared with the theoretical data available on the excited states of CO_2, CO, and O in order to answer the question of coexistence of CO and O in the same matrix cavity. As mentioned in the Introduction, EET can occur through resonant or nonresonant processes. The resonant process is also known as the Förster–Dexter mechanism (especially in organic photophysics and photochemistry). In a Förster-type energy-transfer process, which is of dipole–dipole nature, the following aspects should be fulfilled. (a) The excitation energy of the acceptor should be less than or equal to the excitation energy of the donor. (b) The donor and the acceptor can be well separated from each other, but oscillator strengths of the relevant electronic excitations in both the donor and the acceptor should be significantly large. (c) Spin multiplicities of the donor and the acceptor should remain the same before and after the energy-transfer process.

Even if we leave the excitation bands of CO between 200 and 160 nm (Figure 1 insert), which will be discussed in the following section, the first vibronic band due to the $A^1\Pi(v' = 0) \leftarrow X^1\Sigma^+(v'' = 0)$ transition in CO lies at 156.4 nm. The energy at this wavelength is less than the excitation threshold of O atoms in Ar matrices at 147 nm[33] in order to observe the SD emission. The lifetime of CO in the $A^1\Pi$ state is estimated to be about 10 ps,[35] whereas in the $a^3\Pi$ state it is 7.2 ms in Ar matrices.[31f] Thus, it is very unlikely that a Förster or Dexter type energy transfer occurs from the A state of CO. In addition, the energy transfer is spin-forbidden if $O(^3P)$ is excited directly to $O(^1S)$ irrespective of which excited state of CO is involved in the Förster-type process.

According to the Wigner–Witmer spin conservation rule,[42] the following energy-transfer processes are allowed:

$$CO(A^1\Pi) + O(^3P) \rightarrow CO(X^1\Sigma^+) + O(^3S) \qquad (a)$$

$$CO(A^1\Pi) + O(^1D) \rightarrow CO(X^1\Sigma^+) + O(^1S) \qquad (b)$$

$$CO(A^1\Pi) + O(^3P) \rightarrow CO(a^3\Pi) + O(^1S) \qquad (c)$$

$$CO(a^3\Pi) + O(^3P) \rightarrow CO(X^1\Sigma^+) + O(^5S) \qquad (d)$$

$$CO(a^3\Pi) + O(^3P) \rightarrow CO(X^1\Sigma^+) + O(^3S) \qquad (e)$$

$$CO(a^3\Pi) + O(^3P) \rightarrow CO(X^1\Sigma^+) + O(^1S) \qquad (f)$$

$$CO(a^3\Pi) + O(^1D) \rightarrow CO(X^1\Sigma^+) + O(^3S) \qquad (g)$$

Processes a, d, e, and g are energetically unfavorable, since the available energy of 5.96 eV ($a^3\Pi$) or 7.9 eV ($A^1\Pi$) from CO[34,35] is not sufficient for $^3S \leftarrow {}^1D$ (7.1 eV), $^5S \leftarrow {}^3P$ (9.5 eV), or $^3S \leftarrow {}^3P$ (9.1 eV) excitations in the O atom.[43] On the same grounds, process c can be ruled out as the energy difference between the states $A^1\Pi$ and $a^3\Pi$ of CO (~2 eV), which is much smaller than between the ^1S and ^3P states of O (~4.2 eV).[31,44] So far, no experimental or theoretical evidence is available for the stability of $O(^1D)$ in rare-gas matrices and the Förster-type process b can be eliminated for this reason.

The remaining process f is a Dexter-type exchange process. This kind of energy transfer is efficient only when CO and O coexist in the same cavity and because of the exponential decay of the energy-transfer efficiency with CO···O distance.[2] For the following reasons, this type of exchange energy transfer can also shown to be inapplicable. It should be noted that after direct excitation of CO into the $A^1\Pi$ state, several radiative processes occur that result in hot emission bands between 400 and 900 nm[34,35] from the higher triplet manifold (e, d, and a′ states) to the $a^3\Pi$ state (Figure 5). If CO and O occupy the same cavity and if the Dexter-type energy transfer (*f*) were to occur, then we should have seen broad A ← X excitation bands of CO as a consequence of perturbation of CO by O (Figure 3a), irrespective of which emission band was monitored, i.e., hot emission of CO or the SD emission of O. However, we observe broadening of the bands only when the SD emission of O is monitored. It may be concluded that CO, which forms a geminate pair with O in an Ar cavity, can only transfer the excitation energy to O, resulting in the SD emission of O, but does not show any hot emission between 400 and 900 nm. On the other hand, only those CO molecules that are not surrounded by O show hot emission bands. On the basis of the analysis discussed here, we rule out the Förster–Dexter mechanism as being responsible for the observed energy-transfer process.

Photochemically Induced Electronic-to-Electronic Energy Transfer. As discussed above, we propose that those CO and O species that are responsible for the energy-transfer process coexist in the same parent cavity. To understand why the geminate CO···O pair does not recombine to CO_2, it is necessary to know the site structure around CO_2 in the Ar lattice. IR spectroscopic studies of Irvine et al.[45] have shown that over a wide range of guest–host ratios (1:10000 to 1:320), CO_2 occupies two major sites in the Ar lattice with nearly equal occupancies (1:1). These sites are a single substitutional (SS) site, where one Ar atom is displaced by CO_2, and a double substitutional (DS) site, where two Ar atoms are displaced by one CO_2. The DS site, having more cavity volume, can accommodate geometrical deformations in CO_2 better than the SS site. In the first two excited states, namely, the $^3B_2$ and the $^1B_2$, CO_2 is bound in a bent geometry and is dissociative in its linear geometry.[27] After an initial excitation between 120 and 106 nm, some of the excited CO_2 molecules may relax through radiative or nonradiative processes to the ground state. The rest of the excited molecules dissociate, resulting in CO($X^1\Sigma^+$) and O(^1S) followed by SD emission of O at 558 nm. In a DS site, it is logical to expect recombination of CO(X) and O(^1D or ^3P), resulting in CO_2 in the $^1B_2$, $^3B_2$, or $^1A_1$ states and eventually in the X state (Figure 5). In a SS site such a recombination may be hindered. In addition, a small portion of O atoms leave the mother cage, as also found in the present study (Figures 1 and 3). From these considerations, it is reasonable to assume that only 50% of the CO_2 are accessible for permanent dissociation. Derivation of quantitative information from the excitation spectra measured between 120 and 100 nm is further complicated by the excitation bands of the photoproduct CO as mentioned in the discussion of CO_2 spectra earlier. Based on these facts, the photostationary state reached at 25% photolysis of the CO_2 molecules in 3000 s is reasonable.

We have seen that photolysis of CO_2 between 120 and 106 nm results in O(^1S), which radiatively relaxes to O(^1D). If every O(^1S) or O(^1D) leaves the mother cage, then we have to invoke the Förster−Dexter mechanism to explain the energy-transfer process, which has been shown to be impertinent. Hence, a part of the geminate pairs of CO and O should remain in the mother cage, most probably in the SS sites as indicated above. In the gas phase, it has been shown that O(^1D) is deactivated by CO through electronic-to-vibrational (E−V) energy transfer from O to CO.[30] Thus, after SD emission, O(^1D) would be deactivated to O(^3P) in the presence of CO. As a result CO($X^1\Sigma^+$) and O(^3P) remain adjacent to each other in the Ar cavity. In the gas phase these two species could have reacted in the presence of a third species (an energy sink) to generate CO_2 in its first triplet state ($^3B_2$).[27] As mentioned earlier, in a SS site where the cavity does not permit the formation of a bent CO_2, CO($X^1\Sigma^+$) and O(^3P) have no other choice but to remain as a van der Waals contact pair in the mother cage. It is known[30] that $CO_2(X^1\Sigma_g^+)$ is energetically stabilized by 5.5 eV compared to CO($X^1\Sigma^+$) + O(^3P). An important consequence of this energy difference is that we can access the electronic states of CO_2 with a linear geometry that lie at $x + 5.5$ eV by exciting CO with a photon of x eV energy (Figure 5). It is less important to know which final state of CO_2 can be reached by exciting CO as long as that state relaxes to the dissociative valence state $^1\Sigma_u^+$ (Figure 5). According to the available theoretical data on the excited states of CO_2,[27] this molecule has a linear geometry in the $^{1,3}\Pi_u$ states and it is most likely that O(^3P) and CO($a^3\Pi$) or CO($A^1\Pi$) recombine to result in CO_2 in the $^{1,3}\Pi_u$ states. It is known from the gas-phase studies[26,29,30] as well as from the present work (Figure 1) and the data of Taylor et al.[32] that dissociative excitation to the $^1\Sigma_u^+$ state can be achieved with wavelengths shorter than 120 nm (∼10.5 eV). Thus, excitation of CO($X^1\Sigma^+$) to any electronic state that lies above ∼5 eV should result in the chemical recombination of CO* and O(^3P) to CO_2*, which subsequently relaxes to $CO_2(^1\Sigma_u^+)$ and then dissociates along the asymmetric stretch coordinate to CO($X^1\Sigma^+$) and O(^1S).[26d,27a] O(^1S) emits a photon at 560 nm and relaxes to O(^1D), which through E−V energy transfer[30] with CO($X^1\Sigma^+$) attains its ground state (^3P). The CO($X^1\Sigma^+$) and O(^3P) geminate pair thus participate in *photochemically induced electronic-to-electronic energy transfer* upon excitation of CO. From the excitation spectra measured by monitoring the SD emission of O (insert in the top part of Figure 1) we have found that the EET can be observed starting from excitation of CO into $a^3\Pi(v' = 2)$ at about 6.4 eV, setting a threshold of 11.9 eV with respect to the ground-state CO_2 in order to observe the EET from CO to O.

Excitation Spectrum between 200 and 160 nm. The excitation spectrum between 200 and 160 nm of CO, by monitoring the SD emission of O at 560 nm, is shown as an insert in Figure 1a. It can be interpreted as follows. These bands are much broader, because of perturbation of CO from O, than those obtained by Bahrdt and Schwentner[34b,35] in the same region. The bands at 194 and 188 nm coincide exactly with $v' = 2$ (194.37 nm) and $v' = 3$ (189.24 nm) of the $a^3\Pi(v') \leftarrow X^1\Sigma^+(v'' = 0)$ transition in CO observed by Bahrdt.[35] Between 175 and 158 nm several excitation bands have been reported by Bahrdt and Schwentner[34b] that correspond to $d^3\Delta \leftarrow X^1\Sigma^+$ and $a'^3\Sigma^+ \leftarrow X^1\Sigma^+$ excitations. The same transitions should be responsible for the unresolved broad excitation band observed between 175 and 160 nm in the present study.

Comparison with Earlier Experiments. Fournier et al. have noted in their publication[31c] that no recombination of O atoms had been observed when CO_2 was photolyzed with 8.4 eV light in Ar or Kr matrices. Only when the matrices were warmed was thermoluminescence due to combination of O atoms to O_2 observed by these authors. In the present study O_2 is also produced during the photolysis, which upon excitation between 200 and 100 nm results in an $A' \rightarrow X$ emission band progression between 350 and 700 nm (Figures 2 and 4) in addition to thermoluminescence of O_2 upon annealing of the matrices. This difference between our observation and that of Fournier et al. could be due to the following reasons. In the present study excitation energy is varied between ∼6 and 12 eV (200−100 nm) and the flux of the exciting synchrotron light is much stronger than that employed by Fournier et al. at 8.4 eV. As can be seen from Figure 5, excitation of CO_2 with 8.4 eV energy can produce O(^1D) atoms only. Some of the O(^1D) atoms may remain in the mother cage as CO···O van der Waals complexes and get deactivated to O(^3P) through E−V energy transfer.[29,30] Excitation at 8.4 eV with a weak light flux may not lead to long-range mobility of O atoms to form O_2.[33] On the other hand, excitation with photons of energy up to 12 eV with intense synchrotron light could result in long-range mobility of O atoms that eventually form O_2.

Although excitation at 8.4 eV produces only O(^1D) but not O(^1S), Fournier et al. have observed the SD emission of O.[31] These authors interpreted this observation as due to the absorption of a second photon of 8.4 eV energy through the O(^1S) ← O(^1D) excitation that is made possible by the interaction of O with rare-gas atoms in the matrix,[31d] followed by SD emission. Our recent experiments[33] show that excitation of O(^3P) with a threshold of 147 nm (∼8.4 eV) results in SD emission of O in Ar matrices when O_2 or N_2O molecules are used as precursors. The observation of Fournier et al. using CO_2 as the precursor molecule may neither be due to the O(^1S) ← O(^1D) excitation nor be due to direct excitation of O(^3P). The absorption cross section of CO due to the $A(v' = 3) \leftarrow X(v'' = 0)$ at 146.6 nm is much stronger than the direct excitation of O that is produced through the photolysis of CO_2 in Ar matrices (Figure 1). Excitation at 8.4 eV (147.6 nm, bandwidth unspecified[31]) can result in photolysis of CO_2 through the first photon to generate an intracage geminate CO···O contact pair. Excitation of CO through the second photon leads to photochemically induced E−E energy transfer discussed in the present article from CO to O followed by the SD emission of O at 561.5 nm observed by Fournier et al.

Conclusions

Photochemically induced electronic-to-electronic energy transfer from CO to O presented here is one of the rare examples of spectroscopic observation of such processes and the first of its kind under matrix-isolated conditions. A unique interplay among the potential energy hypersurfaces, cage effect of the matrix, and atomic nature of the energy acceptor allowed us to observe the energy transfer. However, there are some unanswered questions pertinent to CO_2 itself: (a) the electronic spectrum and its assignment in rare-gas matrices, (b) the definite assignment of the valence and Rydberg states that correlate to $O(^1S)$ in the region between 120 and 100 nm, and (c) the potential energy hypersurfaces of the higher excited states. Further theoretical and experimental work in this direction is warranted. Similarly, much more theoretical work at the *ab initio* level is needed in order to quantify the interaction between a rare-gas host lattice (or atoms) and atomic or molecular impurity species. Quantitative information on the potential energy hypersurfaces of these species (for example, O[31,46]) in rare-gas lattices, which is important for understanding their spectroscopic behavior under matrix-isolated conditions, can only be obtained when the rare-gas lattice or at least the first shell surrounding the contact pair or impurity is also taken into account in *ab initio* calculations.

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