

Electron-impact desorption of metastable particles from CO films

H. Shi, P. Cloutier, and L. Sanche

*Groupe du Conseil de Recherches Medicales en Science des Radiations Faculté de Médecine,
Université de Sherbrooke, Sherbrooke, QC, Canada J1H 5N4
E-mail: lsanche@courrier.usherb.ca*

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The impact of monochromatic low-energy electrons (4–52 eV) is found to induce desorption of metastable particles (MP) from multilayer films formed by condensing CO gas on a Pt(111) substrate held at 20 K. The results are compared with metastable production from gaseous CO. Metastable CO (CO*) is identified as the major desorbed species, its desorption is discussed in terms of intramolecular to molecule-surface vibrational energy transfer. Primary electronic excitation proceeds via the states, $a^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$, $I^1\Sigma^-$, and $D^1\Delta$ which contribute to MP desorption directly or by first decaying in high vibrational levels of the $a^3\Pi$ configuration. The energy threshold of 8.0 eV for CO* desorption indicates that CO in low vibrational levels of the $a^3\Pi$ state does not desorb. Electronic excitation occurs either near the surface of the CO film or in the bulk. In the latter case, excitonic motion to the surface can be followed by CO* desorption.

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1. Introduction

Desorption from surfaces induced by electronic transitions (i.e., DIET) is a complex process which proceeds through a variety of steps including primary excitation, evolution of electronic excitation (propagation, localization, and on-site evolution, etc.) and coupling of the electronic excitation to nuclear motion [1]. While rather detailed knowledge about DIET from rare gas solids has been obtained [1], DIET of neutrals from molecular solids is not so well documented due to the additional channels involving coupling of rovibrational internal energy to the translational energy of the desorbing particle.

It is known that molecules are commonly produced and desorbed by electronic excitation on grains in interstellar media as well as on comet [2]. CO is a common molecule in the interstellar medium and a significant component in stellar and planetary atmospheres and comets [3]. CO is chosen here in our effort to understand DIET of cryogenic molecular solids. The selective detection of metastable particles (MP) provides a possibility for isolating particular processes. We report high-resolution excitation functions and time-of-flight (TOF)

distributions of MP desorbed from low-temperature CO films by electron impact, with comparison to metastable production of gaseous CO, in order to determine the initial electronic excitation, the desorption species and their kinetic energy. It is suggested that several vibrational excited CO* states contribute to the measured MP signal through intramolecular to molecule-surface vibrational energy transfer.

2. Experiment

The experiment was performed in an ultra-high-vacuum system reaching a base pressure of $\sim 10^{-10}$ Torr. The apparatus has been described in detail previously [4]. A well-collimated low-energy (0–52 eV, $\Delta E = 60$ meV) electron beam impinges on a Pt(111) single-crystal at 18° with respect to the surface normal; the desorbed charged particles are repelled by concentric grids, whereas UV photons and desorbed MP passing through the grids are measured with a large area micro-channel plate array superimposed on a position-sensitive anode. The electronic energy threshold for the MP detection is estimated to lie slightly below 6 eV, from the fact that N_2^* in the $A^3\Sigma_u^+$ and CO* in the $a^3\Pi$ states

can be detected by the micro-channel plates [4,5]. The energy of the vacuum level is calibrated ± 0.3 eV by measuring the onset of the target current as the voltage between the electron source and the target is slowly increased. The crystal, which is mounted on the tip of a closed-cycle helium cryostat, can be cooled to 20 K and cleaned by electrical heating and Ar bombardment. The target films are grown on the Pt(111) surface by dosing CO gas with a purity of 99.99%. The CO thickness is determined with an uncertainty of $\pm 50\%$ and a reproductivity of $\pm 10\%$ [4].

TOF measurements are performed by switching on the electron beam on for 10 μs and subsequently recording the arrival time of those particles which trigger the microchannel plates. Emission of UV photons produces a peak at $t = 0$ followed by the arrival of the MP. The path length (d) between the target and the detector is 5.2 ± 0.1 cm. This parameter is related to the kinetic energy $E(t)$ of the metastable particles by the relation

$$E(t) = \frac{M}{2} \left(\frac{d}{t} \right)^2 \quad (1)$$

where M is the mass of the metastable-particle (28 amu for CO) and t is the time of flight. From this relation, we find the resolution in translational energy

$$\Delta E(t) = \frac{Md}{t^2} \left(\Delta d + \frac{d}{t} \Delta t \right). \quad (2)$$

3. Previous work on metastable production from CO

Our present knowledge on metastable production from CO by electron impact has been obtained essentially from gas-phase experiments. A summary of these studies is given here to facilitate the interpretation and discussion of our results in the next section. Our approach can be rationalized by the general similarities between the gas phase and the solid [6,7]. Electron impact excitation of CO in CO films shows that the band positions are shifted to the red by only a few tenth meV, and the intensity distributions in the progressions are well represented by the gas phase Franck-Condon factors [7]. This is also true of CO excitation in light rare gas (Ne, Ar) matrices [6]. Lifetimes of excited CO states are shortened in Ne matrices due to nonradiative relaxation [6], but they are not far from the radiative lifetimes in the gas phase.

Gas phase lifetimes of some CO excited states are listed in Table. The lowest electronic excited state ($a^3\Pi$) has a lifetime of 1 to 60 ms [8,9]. This state

has been found to provide the dominant contribution to the total cross section for production of metastable CO by electron impact [15]. The $X^1\Sigma^+ \rightarrow a^3\Pi$ transition is a spin-forbidden transition and the $a^3\Pi$ state is excited by an electron exchange process or/and cascading from higher excited states. $a^3\Pi$ production has a threshold at about 6 eV, goes over a maximum located at 9 to 10 eV, and then decreases continuously with electron energy [8,15–17]. By direct observation of the Cameron Band system, Ajello reported that the maximum electron-impact cross section for $a^3\Pi$ at about 11 eV has a value of $1.1 \cdot 10^{-16}$ cm² [16]. The value of the peak cross section was reanalyzed and raised to $1.5 \cdot 10^{-16}$ cm² [17]. Excitation of the $a^3\Sigma^+$ and $d^3\Delta$ states, with lifetimes of several μs [10], as well as the $b^3\Sigma^+$ state can contribute to the metastable excitation function via the $a^3\Pi$ state [15]; i.e., through $a^3\Sigma^+ \rightarrow a^3\Pi$, Asundi bands, $d^3\Delta \rightarrow a^3\Pi$ triplet bands and $b^3\Sigma^+ \rightarrow a^3\Pi$, the third positive band.

Table

Lifetimes of some CO excited states in the gas phase

CO state	$a^3\Pi$	$a^3\Sigma^+$	$d^3\Delta$	$e^3\Sigma^-$	$b^3\Sigma^+$	$I^1\Sigma^-$ and $D^1\Delta$
Life-time	1–60ms ^a	4–10 μs ^b	3–7 μs ^b	3–8 μs ^b	60ns ^c	80 or 97 μs ^d , up to 1s ^e

^a From Refs. 8 and 9; ^b from Ref. 10; ^c from Ref. 11; ^d from Refs. 12 and 13; ^e from Ref. 14.

A higher lying metastable state at around 10 eV has been observed by several investigators [8,12,13, 18–20]. Olmsted et al. [18], using a silver-magnesium alloy surface detector, observed a strongly rising cross section with an onset at 10.5 eV and estimated the lifetime of this metastable states to be of the order of 100 μs . They proposed that this might be the $b^3\Sigma^+$ state. Using Penning-ionization detection, Cermak [20] established the existence of two metastable states, one with an energy in the range 9.2–10.2 eV and the other with an energy ≥ 10.2 eV. Borst and Zipf [8] derived the excitation cross section of the higher lying state by subtracting from the total excitation cross section the cross section of the $a^3\Pi$ state, observed by Ajello [16], giving a threshold at 10.4 eV. They estimated the lifetime to be 150 μs , and precluded the $b^3\Sigma^+$ state, which has a lifetime of 60 ns [11]. Later, Wells et al. [12] located the threshold at 9.5 eV and determined the state's lifetime to be 97 μs at 15 eV. They also deduced an electron impact cross section of

$3 \cdot 10^{-18} \text{ cm}^2$ at 15 eV and proposed the $D^1\Delta$ and $I^1\Sigma^-$ states as possible metastable states.

Mason and Newell [13] isolated the higher lying metastable state from the influence of the $a^3\Pi$ state by using a channel electron multiplier having a work function of about 8 eV. The threshold excitation energy was determined to be 9.45 eV and the lifetime was deduced to be 80 μs for incident energies between threshold and 35 eV which slightly decreases to 70 μs at electron energies above 40 eV. Maximum cross section was evaluated to be $3 \cdot 10^{-18} \text{ cm}^2$ at 16 eV. They assigned the MP production to direct excitation of the $I^1\Sigma^-$ state.

Electron impact on CO can also result in the formation of metastable carbon and oxygen atoms from dissociative excitation. Wells et al. [21] observed metastable fragments composed of long-lived high-Rydberg carbon and oxygen atoms and $O(^5S^0)$ atoms with kinetic energies ranging from 0 to 25 eV, for impact energies in the range of 0 to 300 eV. Eight discernible TOF peaks were observed. The lowest appearance potential was found at 20 eV. An electron-impact cross section of $2 \cdot 10^{-18} \text{ cm}^2$ at 190 eV was deduced for the production of metastable fragments assuming that O^* , C^* , and $O(^5S^0)$ have equal cross sections. Barnett et al. [22] found only one peak in kinetic energy distributions for the metastable oxygen fragments from carbon monoxide. The peak kinetic energy increases from 3.75 at 40 eV to 4.69 at 60 eV. LeClair et al. [23] detected $O(^1S)$ production with a threshold at 16 eV and a maximum cross section of $5 \cdot 10^{-19} \text{ cm}^2$ at 100 eV.

Becker et al. [24] investigated Cameron bands luminescence from CO-doped solid Ar using synchrotron radiation and thermally stimulated luminescence. They observed weak lines at 8 eV in the excitation spectrum which corresponds to direct photoexcitation of the matrix isolated CO by spin-allowed singlet transitions $X^1\Sigma^+ \rightarrow A^1\Pi$. Electronic excitation of CO by energy transfer from excitons of the matrix was seen between 12–14 eV. They attributed the strong increase in luminescence just above 21 eV as due to $CO^*(a^3\Pi)$ production by inelastic scattering of low-energy photoelectrons. In the same system, Bahrtdt et al. [25] found a CO metastable state at about 11 eV with a lifetime of about 15 ms. It was assigned to a CO quintet state populated nonradiatively after excitation of a Rydberg state.

Thresholds for electron stimulated desorption (ESD) of neutral (ground-state + metastable) molecules from several molecular solid films, including solid CO, were reported by Rakhovskaia et al. [26].

Desorption thresholds appeared at distinct electron energies: for CO it was about 6 eV and assigned to excitation of the $a^3\Pi$ state. ESD signals below the electronic excitation threshold were smaller by a factor of 250. The desorption mechanism is believed to be conversion of electronic to vibrational and finally to translational energy via radiationless decay. More recently, Scheuer et al. [27] and Wurm et al. [28] investigated the correlation of internal excitations and substrate-adsorbate coupling for CO molecules desorbed from metallic and Xe surfaces by 150 eV electron impact. They attributed the strong yield of desorbed ground state CO in high vibrational states to quenching, by the metal substrate, of CO^* molecules which are dissociative with respect to both the C-O bond and the molecule-surface bond.

Desorption of ground-state neutrals from solid CO also has also been investigated by excitation with energetic ions [29,30]; the yield was found to have a quadratic dependence on the electronic stopping power of the incident particles. Chrisey et al. [30] concluded that this dependence is intrinsic to the electronic energy conversion process in CO, i.e., intrinsic to the energy transfer process which sets molecules in motion. However, they did not identify the molecular state involved.

Low energy electron stimulated MP desorption has been investigated in our laboratory for various condensed films [4,31–33]. In the case of CO, only the yield function of MP desorption for a 50 monolayer (ML) film has been reported between 5 and 19 eV [32]. In this paper, we report the results of experiments performed on the thickness dependence of the MP yield within the 4–52 eV electron energy range, and those obtained from the TOF distributions recorded at different impact energies within that range.

4. Results

The metastable yield functions of CO films are shown in Fig. 1 for various CO thicknesses. The curves are similar in shape for film thicknesses larger than 2 ML. For all CO thicknesses, there is a common MP desorption threshold at 8.0 eV, and the yield increases continuously with electron energy, exhibiting a broad peak at about 16 eV. These results are in agreement with those previously reported for 5–19 eV electrons impinging on a 50-ML CO film [32].

TOF distributions of desorbed MP were measured with different incident electron energy within the 10 to 50 eV range. Apart from the small but sharp peak at $t = 0$ due to UV photon emission,

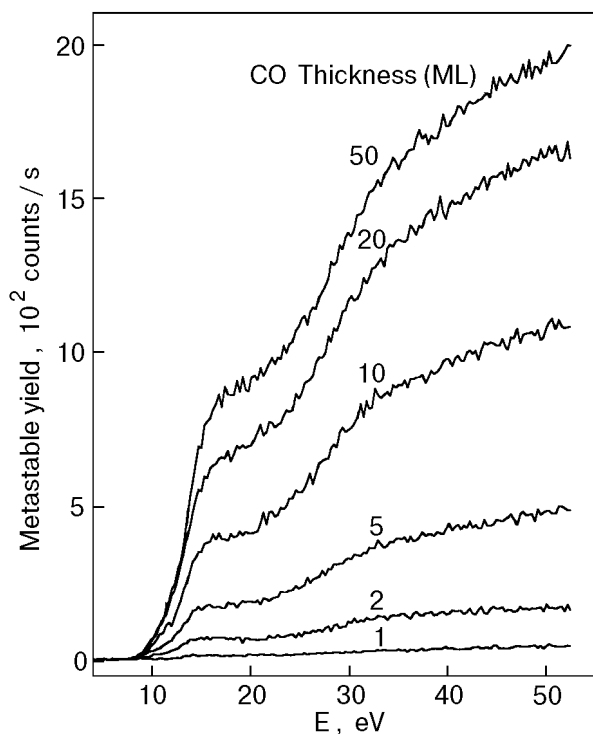


Fig. 1. Metastable carbon monoxide (CO^*) desorption yields induced by 4–52 eV electrons impinging on CO films of different thicknesses indicated in monolayers (ML).

each distribution exhibits a single TOF peak; the line shape of all distribution curves are very similar to each other. In Fig. 2, TOF results are shown for a 50-ML CO film for incident energies of 11, 15 and 50 eV, while the integrated peak area is plotted in the insert as a function of electron energy. The later reproduces very well the shape of the metastable yield functions recorded for thicknesses larger than

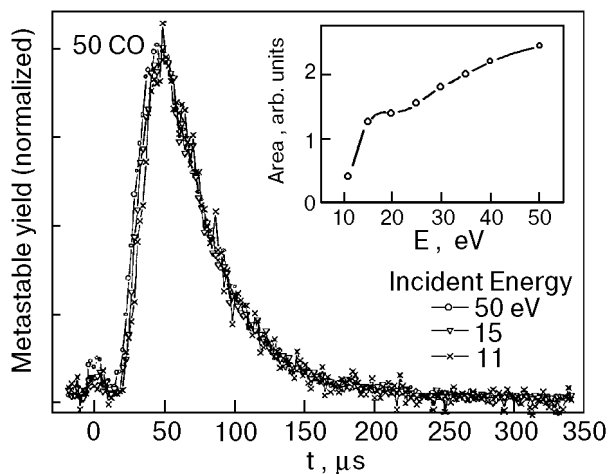


Fig. 2. Normalized time of flight (TOF) distributions of CO^* desorbed by the impact of 11-, 15-, and 50-eV electrons on a 50-ML CO film. The integrated TOF peak area is shown in the insert as a function of incident electron energy.

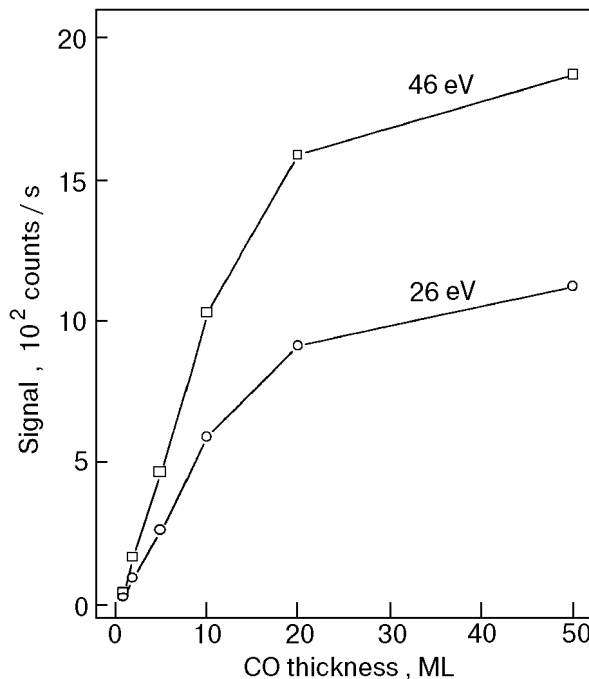


Fig. 3. CO^* signal intensity as a function of CO thickness, deduced from Fig. 1.

2 ML shown in Fig. 1. The MP distribution peak at about $45 \pm 5 \mu\text{s}$ corresponds to a kinetic energy of $195 \pm 50 \text{ meV}$ for CO^* . With increasing electron energy, there is a slight shift in the rising slope of TOF distributions which indicates that higher energy MP are being fed into the distribution with increasing electron energy. The yield of CO^* as a function of film thickness is shown in Fig. 3 for incident electron energies of 26 and 46 eV.

5. Discussion

Below the electron energy of 20 eV, any detected MP signal should arise from metastable carbon monoxide (CO^*). Although LeClair et al. [23] detected an onset for the production of $\text{O}(^1S)$ at 16 eV, the internal energy of this state of 4.17 eV is too low to trigger our MP detector. The $\text{O}(^5S^0)$ state possesses an excitation energy of 9.14 eV and a lifetime of 180 μs , but it is not produced below 20 eV [21]. The threshold energy of 8 eV shown in Fig. 1 is higher than that of 6 eV for the metastable ($a^3\Pi$) production for gaseous CO [8,15]. It indicates that no significant quantities of CO in the $a^3\Pi$ state desorb from a CO film for impact energies between 6–8 eV. Thus, the threshold corresponding to $a^3\Pi$ excitation reported by Rakhovskaia et al. [26] in the neutral CO desorption yield from solid CO must arise essentially from CO molecules in their ground state.

At low electron-impact energies, the desorption process must be simple since ionization, desorption of dissociation fragments, and desorption via collision cascade can be excluded. There are only three possibilities for the desorption of excited molecules from a molecular solid at low energies. In one case, the excited molecule at the surface has an energy higher than in the gas phase. Motion along a repulsive molecule-surface potential-energy curve can lead to acceleration and desorption of the excited molecule. This is called the cavity expulsion mechanism. In crystals with a positive electron affinity, the excited particle is not expelled owing to the attractive interaction of the excited-orbit electron cloud with the neighboring atoms. Solid CO has a positive electron affinity [34] which rules out MP desorption through cavity expulsion [35]. Another possibility is local repulsive CO*-CO interaction near the film surface which could lead to CO* ejection in vacuum (dimeric ejection). This is impossible at low energies for CO because all of the valence CO excited states lie at lower energies in condensed CO than in gaseous CO [7]. The only possibility left is desorption via intramolecular to molecule-surface vibrational energy transfer. Direct excitation to the $a^3\Pi$ state only produces low intramolecular vibrational quanta ($v = 0-4$) [7] which may not allow sufficient energy transfer to the molecule-surface bond during the lifetime of the state to induce desorption [36]. This may explain the lack of CO* desorption in the 6-8 eV range.

For a given electronic transition, the vibrational population of the CO molecules is determined by the Franck-Condon factors. From potential-energy diagrams of CO and known molecular constants [37], excitation to the $a^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$, $I^1\Sigma^-$, and $D^1\Delta$ states is expected to be in high vibrational levels. Rosenkranz and Kirby [14] calculated the Franck-Condon overlaps which peak at $v = 14$ and 15 for the I and D states, respectively. For the $a^3\Sigma^+$ state, vibrational levels $v = 7-24$ lie within the Franck-Condon region, the $v = 8$ level corresponds to our threshold of 8 eV for metastable CO desorption observed in the present experiment. According to the near-threshold excitation spectrum of CO multilayers [7], the $a^3\Sigma^+$ state is the only one produced with a non-negligible amplitude by 8-10-eV electrons. We therefore ascribe the MP yield in the range 8-10 eV to initial excitation to that state. Above 10 eV, the $d^3\Delta$, $e^3\Sigma^-$, $I^1\Sigma^-$, and $D^1\Delta$ states can also be excited by electron impact and therefore they are expected to be involved in MP desorption.

The CO* molecules may desorb directly in these states or first decay into high vibrational levels of the $a^3\Pi$ configuration, depending on the rate of energy transferred from intramolecular vibration to the molecule-surface bond. This energy transfer is thus strongly dependent on the lifetime of the initial excited state [38,39], but also on the amount of librational motion and vibrational energy of the excited molecule [36] and the surface temperature. CO with its high vibrational frequencies and small rotational constants has long vibrational relaxation times in the ground state, ranging from milliseconds to seconds depending on environment and other parameters [40]. Since the nonradiative contribution to the relaxation process is multiphonon [41], we may expect energy transfer to molecular-surface bond to have similar time scales. However, in the excited states, the higher vibrational energy content and the stronger molecule-surface bond may lead to shorter times for such a transfer. In fact, recent three-dimensional quantum calculations on CO physisorbed on a NaCl(100) rigid surfaces [36] show that significant desorption of the molecule can occur within picosecond times for initial librational quanta as small as 2, provided translational motion due to temperature is taken into account. Unfortunately, no such calculation exists for the case of CO on CO at cryogenic temperatures which would allow to determine if the lifetimes given in Table are sufficient for desorption of CO* before decay to the $a^3\Pi$ state, when all the factors previously mentioned are taken into account. Although it is well established that CO desorption can occur as the result of energy transfer from intramolecular to molecule surface desorption modes, we cannot with present experimental and theoretical evidence determine the state of desorption of CO*. We therefore limit our discussion to the configurations which are initially excited by electron impact. In any case, CO* is likely to reach our detector in the $a^3\Pi$ configuration. The other triplet states, having lifetimes of several μs [10], can be radiatively de-excited into the low-lying $a^3\Pi$ state during the TOF. The lifetimes for $I^1\Sigma^-$ and $D^1\Delta$ states were measured to be 80 or 97 μs , respectively [12,13], but the lifetimes of the low-lying vibrational levels of these states are very long (up to 1 s) due to the small transition energies to the $A^1\Pi$ state [14]. Since the desorption by vibrational energy transfer lowers the vibrational levels of desorbed CO*, it may be possible that the desorbed metastables in I and D states live sufficiently long (presumably several hundred μs) to arrive at the detector.

Using the R-matrix method, Morgan and Tenynson [42] have calculated electron-impact excitation cross sections for the lowest seven electronically excited states of CO in the energy range 6–18 eV. A sharp electron resonance feature (${}^2\Pi$) is found at 10.4 eV for the $a'^3\Sigma^+$ configuration, and the $d^3\Delta$ results show a shoulder at about 11 eV due to a ${}^2\Phi$ resonance [42]. For energy above 12 eV, the cross sections for the $a'^3\Sigma^+$, $d^3\Delta$, and $e^3\Sigma^-$ states are in the same order of magnitude while for the $I^1\Sigma^-$ and $D^1\Delta$ states, they are about 5 times smaller. Interestingly, they have compared the excitation of the higher metastables $I^1\Sigma^-$ and $D^1\Delta$ states with the measurement of Mason and Newell [13] and found roughly the same shape, with a maximum located near 16 eV. Cross sections for the excitation of all metastables, i.e., the a , a' , d , e , I , and D states, exhibits a maximum at 9 eV due to the major contribution from the $a^3\Pi$ state and a second maximum at about 15.5 eV [42]. The first maximum is not expected to be observed in our experiments since it is dominated by direct excitation of the $a^3\Pi$ state which does not directly contribute to MP desorption from CO films. However, considering that the near-threshold electron-impact excitation spectrum of CO is similar in both phases [7], we expect the energy dependence sum of the calculated cross sections of the $a'^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$, $I^1\Sigma^-$, and $D^1\Delta$ states to have roughly the same shape (except the resonance features for the $a'^3\Sigma^+$ and $d^3\Delta$ states) as that of the MP yield function for CO films below 20 eV. We therefore ascribe the broad peak at 16 eV in Fig. 1 to contributions from initial excitation of these states. Above 16 eV, MP yield from a CO film increases further while it decreases for gaseous CO. This difference for solid and gas phase excitation possibly arises from multiple inelastic scattering of electrons in solids.

There is a slight shift in the TOF distributions in Fig. 2 with increasing electron energy. This is not expected from a CO^* signal originating from a single electronically excited state. Thus, the MP signal is believed to arise from an admixture of CO^* configurations whose relative contribution changes slightly with electron energy, assuming that the MP yield at 50 eV is still dominated by molecular desorption. This is in agreement with our discussion that the states $a'^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$, $I^1\Sigma^-$, and $D^1\Delta$ are all possibly involved.

Above 20 eV, metastable carbon and oxygen atoms are observed in CO excitation in the gas phase [21–23]. If produced in highly excited states (e.g., oxygen in the ${}^5S^0$ state) these fragments could be detected in our experiments. Since they are

created with eV's of kinetic energy they are expected to produce a signal between 8–15 μs (4–1 eV) in the TOF distributions, a time domain where the magnitude of the MP yield is minimal. Hence, we suggest that highly excited atoms do not contribute significantly to the MP yields from condensed CO (i.e., the MP signal, produced by incident energy up to 50 eV, is essentially due to CO^* desorption). In the gas phase, however, the cross section for the production of atomic MP is of the order of 10^{-18} cm^2 , which is comparable to that of the production of CO^* in I and D states [12,13, 21–23]. The fact that we do not observe noticeable atomic MP desorption may be caused by preferential deexcitation of highly excited C and/or O atoms in the bulk and near the surface or deexcitation of dissociative states to bound states before complete separation of the C and O atoms, as suggested by Scheuer et al. [27]. Deexcitation of metastable atoms can occur by recombination, by excitation energy transfer between the atomic MP and the CO molecules as well as other radiationless decay and radiative transitions. Some of these processes may involve kinetic energy that induce collision cascade sputtering of neutral (ground-state) CO or desorption of ground state carbon and oxygen atoms, which we cannot detect.

On the other hand, molecular CO^* produced in the bulk is expected to contribute to the MP desorption by exciton motion. Analysis of the data in Fig. 1 indicates that, within the 10–52 eV range, the MP signal increases more or less linearly with CO thickness between 2 and 10 ML; above 10 ML, the rate of increase reduces with a tendency toward saturation above 20 ML. This behavior is shown in Fig. 3 for incident energies of 26 and 46 eV.

Using the mathematical expression developed to explain the dynamics of MP desorption from N_2 films [33], we obtain for a given incident electron energy the following expression for the CO^* yield (Y_d) of a film of thickness T (expressed in ML):

$$Y_d \propto P_d \sum_{L=1}^T \left\{ P_{\text{CO}^*} [M, I_e(L)] f(L) \right\} \quad (3)$$

where P_d is the desorption probability of CO^* at the surface during a given time interval; P_{CO^*} is the probability to form CO^* , which is a function of the electronic excitation matrix elements M and electron beam intensity I_e at a distance L from the surface; $f(L)$ is the exciton-motion function which reflects the probability of an exciton to move to the surface. Comparing the results of Fig. 3 to Eq. (3), we see that Y_d increases with T , indicating a contri-

bution to the MP yield from CO excitation in the bulk. $f(L)$ is necessarily non-zero for CO thicknesses up to 50 ML. Furthermore, these results can be interpreted as due to a CO^* yield directly proportional to the summation of CO layers in Eq. (3), with P_{CO^*} and $f(L)$ being independent of thickness in the range $2 \leq T \leq 10$ ML. The slower increase above 10 ML is probably the results of electron-beam attenuation, which reduces P_{CO^*} , and/or a reduction of $f(L)$.

6. Conclusion

Low-energy electron stimulated desorption of metastable particles from CO multilayer films exhibits a threshold at 8 eV which suggests direct excitation of the $a^3\Sigma^+$ state followed by desorption in either the a' or $a^3\Pi$ state via intramolecular to molecular surface vibrational energy transfer. Similarly, the states $d^3\Delta$, $e^3\Sigma^-$, $I^1\Sigma^-$, and $D^1\Delta$, are believed to be the first excited and contribute to the MP signal by the same energy-transfer mechanism. In this case, desorption may also be preceded by decay into high vibrational levels of the $a^3\Pi$ state. Excitation of CO^* in the bulk also results in MP desorption through exciton motion. Desorption of metastable atoms in highly excited states is negligible in the electron energy range 0–52 eV. Finally, we note that, besides their interest to DIET processes, investigations such as the present one, may also be of value in the interpretation of luminescence data generated by photons [43] or charged particles [44] of sufficient energy to produce low-energy electrons.

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