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Kedzierski, Wladyslaw; Blejdea, E; DiCarlo, Aldo; and Mcconkey, J. W.. (2010). Electron impact dissociation of N₂O and CO₂ with single particle detection of O(1D₂). *Chemical Physics Letters*, 498 (1-3), 38-41.
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Electron Impact Dissociation of N₂O and CO₂ with Single Particle Detection of O(¹D₂)

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Abstract: Production of metastable O(¹D₂) atoms following controlled electron impact on N₂O and CO₂ targets has been studied using a neon rare gas matrix detector operating at a temperature of <20K. A 100 eV pulsed electron beam was used in conjunction with time of flight (TOF) techniques to establish O-atom fragment kinetic energies. Probable dissociation channels are discussed.

PACS #: 34.80 Dp and Ht, 33.20 kf, 37.20 +j, 34.35 +a

Introduction

Metastable $O(^1D)$ atoms are an important constituent of the terrestrial atmosphere. Emission from $O(^1D)$ atoms produces the well known ‘nebular’ red lines at 630 and 636.4 nm in the airglow and auroral spectra. A major source of $O(^1D)$ atoms in the atmosphere is photo-dissociation of O_2 or O_3 by solar ultraviolet photons. Quenching of $O(^1D)$ atoms heats the atmosphere, and chemical reactions of $O(^1D)$ atoms modify its chemical composition, particularly in the stratosphere [1,2]. Beyond earth’s environment, $O(^1D)$ is an active participant in cometary processes [3], and the red lines are prominent features of many nebulae [4]. $O(^1D)$ is also important in any plasma or discharge situation involving oxygen containing gases [5]. N_2O and CO_2 are potential significant sources of $O(^1D)$ in the terrestrial atmosphere.

Observation of $O(^1D)$ in the laboratory is complicated by its long (116 sec) lifetime [6]. Thus, although it is readily possible to excite the red lines in a discharge by using a buffer gas to reduce wall deactivation [7], it is extremely difficult to detect $O(^1D)$ directly. The most successful techniques are laser or synchrotron based, where ionization of $O(^1D)$ is used as a precursor to mass spectroscopic detection of the resultant O^+ , [8,9]. Recently, Kedzierski et al. [10], have demonstrated that it is possible to carry out efficient single particle detection of the other low lying metastable oxygen, $O(^1S)$, using rare gas matrix detectors. When the $O(^1S)$ atom strikes a solid rare gas surface, it immediately forms an RgO^* excimer which promptly radiates. The present report describes the use of one such detector to monitor electron impact dissociative excitation of N_2O and CO_2 with the production of $O(^1D)$.

The evolution of the technique of using excimer formation in a solid rare gas matrix to shorten the lifetimes of metastable atoms has its genesis in earlier work where small quantities of oxygen

containing molecules were frozen out in solid deposits of rare gases and then bombarded with electrons or energetic photons [11-18]. The mechanisms which governed the processes involved were well studied and fairly well understood. Ar and Kr and Xe matrices were observed to give similar photon outputs though with individual spectral signatures. Recently, Kedzierski et al. [10], have discussed how $O(^1S)$ atoms, resulting from molecular break-up and impinging on a solid rare gas surface, (Ne, Ar, Kr or Xe), form similar RgO^* excimers which promptly radiate. This work was a development of earlier work by LeClair and McConkey [19], in our laboratory using a solid Xe surface detector at 65K. Using this single particle detector we were able to study $O(^1S)$ production following controlled electron impact with a large number of oxygen-containing molecules [5].

The resultant excimer radiation is detected by a cooled photomultiplier. By employing pulsed electron beam excitation together with time-of-flight (TOF) techniques, the transit times of the $O(^1S)$ atoms from the interaction region to the rare gas surface were determined and hence their translational kinetic energies. The sensitivities of the different rare gas matrices were investigated as a function of matrix temperature. In all cases, detector sensitivity maximized at temperatures $\leq 20K$. Kr was found to provide the most sensitive surface and Ne the least. Excimer lifetimes were demonstrated to be less than $5 \mu s$ except for the ArO^* species where a lifetime of $23.4 \mu s$ was measured. These lifetimes may be compared with the gas-phase value of $0.74 s$ [20] indicating lifetime reductions by a factor of approximately 10^6 .

The Ne matrix was identified in the earlier work [13,15,21,22] as being different from the other rare gas matrices in that the spin forbidden ($^1D - ^3P$) emission was also observed following VUV photon irradiation of matrices containing traces of O_2 , N_2O or CO_2 . More recently, Belov et al. [23], used 2 keV electron bombardment of Ne crystals containing a trace of O_2 and confirmed

that the ($^1D - ^3P$) emission was observed from the matrix. Mohammed [24] reported that $O(^1D)$ lifetime shortening also occurred if an SF_6 rather than a Ne matrix was used as the host material. All of this suggested that it might be possible to detect 1D directly using a similar technique to that used previously for 1S . This report discusses the results of such an investigation.

We note that numerous investigations have studied photo-dissociation of oxygen-containing molecules, with production of $O(^1D)$, dating back to the early pioneering work of Slanger and Black [25,26]. Stolow and Lee [8] studied the break-up of CO_2 at 157.6 nm using a crossed beam technique and a mass spectrometer detector, and confirmed earlier work, using LIF [27] and chemical scavenging [28] techniques that the dominant reaction pathway at this wavelength was:



with a quantum yield of 0.94 and an angular anisotropy parameter, β , of zero. More recently, Lu et al. [9] obtained similar results using photo-fragment translational spectroscopy where the ionization stage was accomplished using VUV synchrotron radiation. Dunlea and Ravishankara [29] have studied the quenching of $O(^1D)$ by various molecules and Perri et al. [30] have studied the fine detail of this process when the quenching partner is CO_2 . Using REMPI (resonance enhanced multi-photon ionization) techniques, photo-dissociation of N_2O yielding $O(^1D)$ has been studied by Neyer et al. [31] who give reference to earlier work.

Experimental Details

The crossed electron target gas beam system, which has been used previously to study $O(^1S)$ production from various targets, has been described in earlier publications by LeClair and McConkey [19], McConkey et al.[5], Kedzierski et al. [10], and so only salient relevant details

will be given here. CO₂ and N₂O target gases were of 99.99% stated purity and were used without further purification. The metastable atoms, produced by a pulsed electron gun interacting with the gas targets, were allowed to drift through a differentially pumped region and impact a neon matrix deposited on a cold finger at a nominal temperature of 10K. Here they formed NeO* excimers which promptly radiated. A fraction of the resultant photons passed through an isolating red filter and were detected by a cooled photomultiplier. The filter served to discriminate against NeO*(¹S) excimers which were being detected simultaneously but which radiated in the green as shown by Kedzierski et al. [10]. Pulses from the photomultiplier were routed to a multichannel scaler (MCS) where a time-of-flight (TOF) spectrum was accumulated. The zero of the time scale on the MCS was established by the prompt photons which are produced from the excitation of the target particles during the e-beam pulse and subsequently scattered into the photomultiplier from the cold finger.

Results and Discussion

Fig. 1 shows TOF spectra which were obtained using an N₂O target and an electron beam energy of 100 eV. We note that the prompt photon peaks have been suppressed in this diagram for reasons of clarity.

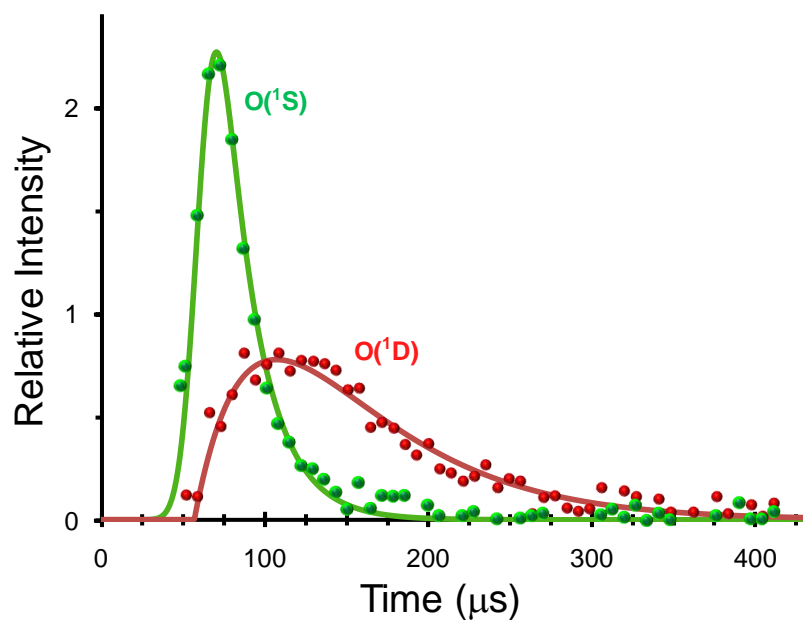


Fig. 1. O(1S) and O(1D) TOF data obtained using 100 eV electron impact on a N₂O target. The e-beam pulse width was 25 μ s and the target driving pressure was 5 torr. Note that the prompt photon peaks at zero time have been suppressed for the sake of clarity. Red and green filters were used to obtain the two different data sets. Data-taking time for O(1D) was much longer than for O(1S) so the two data sets can not be compared directly.

The two TOF spectra are distinctly different emphasizing the fact that they are produced via distinctly different channels. The O(1D) signal was much weaker than the O(1S) signal. This is evident from the fact that the time taken to accumulate the O(1D) spectrum in Fig. 1 was a factor of 3 longer. It is not clear whether the probability of producing O(1D) in the collision is much less or the sensitivity of the neon matrix detector is greatly reduced or some combination of these is occurring.

The $O(^1S)$ TOF spectrum may be compared with earlier data taken in our laboratory using a Xe matrix detector [19,32]. Excellent correspondence between the two data sets is obtained.

Fig. 2 shows similar TOF data but with a CO_2 target. Here again the prompt photon peak has been suppressed for clarity and a large constant background signal has been subtracted from the data. Unfortunately it is not possible to put these data on an absolute cross section scale.

However, comparing the $O(^1D)$ signals with those obtained from N_2O suggests that the production cross section here is about 50% larger. Incidentally, we were not able to observe any $O(^1D)$ signal from O_2 targets. This may not be surprising given the fact that $O(^1S)$ signals from N_2O and CO_2 were about an order of magnitude larger than from O_2 [19,33]. We note that Belov et al. [23], using 2 keV electron bombardment of Ne crystals containing a trace of O_2 observed that the $(^1D - ^3P)$ emission from the matrix had a much lower intensity than the $(^1S - ^1D)$ green band.

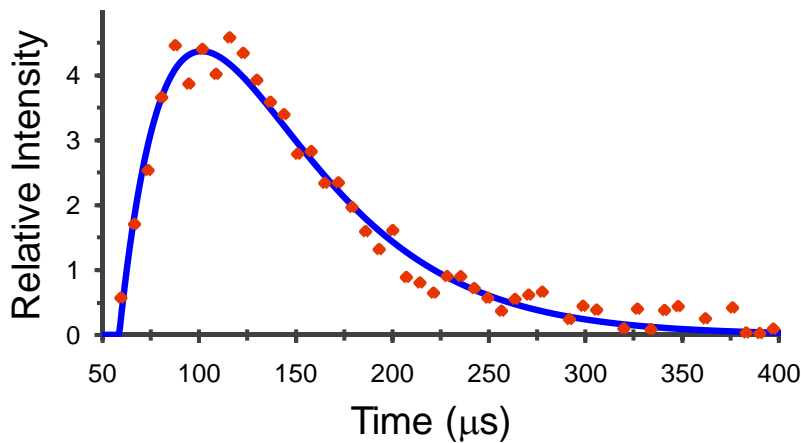


Fig. 2. $O(^1D)$ TOF data obtained using 100 eV electron impact on a CO_2 target. The e-beam pulse width was $25\mu s$ and the target driving pressure was 5 torr. Note that the prompt photon peak at zero time has been suppressed for the sake of clarity. A red filter blocking radiation below 600 nm was used to obtain this data set.

There is no obvious structure present in the TOF, Fig. 2. We contrast this to what was observed, by LeClair and McConkey [33], for $O(^1S)$ production from this target. There, six features were evident following 100 eV electron impact indicating at least this number of channels contributing to the observed signal. Here, the apparent lack of structure may be a product of the poorer statistics and the much broader electron pulse which had to be used in the present work. Thus any structure present in the data could be “washed out”.

Using the curves which have been fitted to the data points in Figs. 1 and 2 together with the known distance between the interaction region and the detector surface, we can convert the data to graphs of signal intensity versus fragment kinetic energy. The result is shown in Fig. 3.

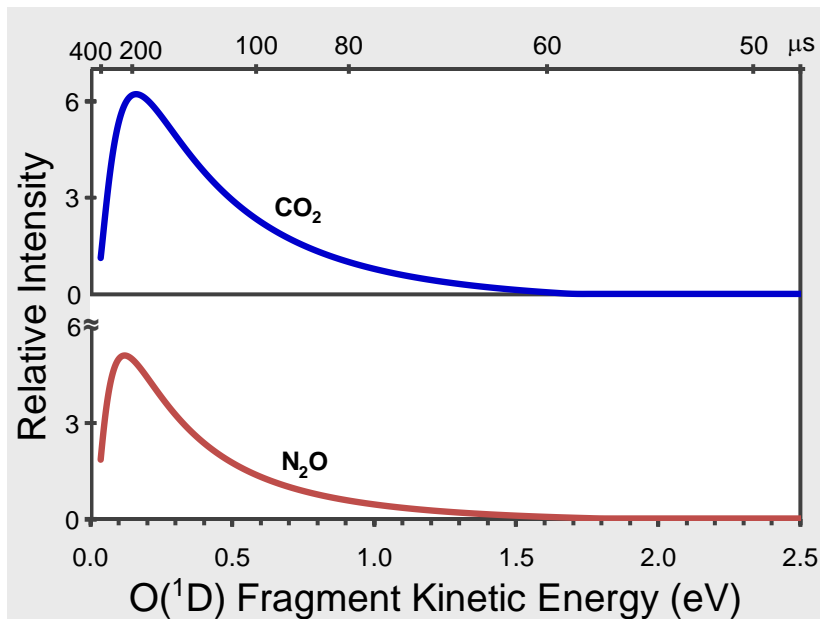
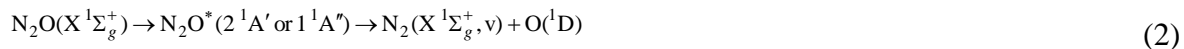


Fig. 3. O-fragment kinetic energy transforms of the data shown in Figs. 1 and 2. The ordinate scales are arbitrary but they do reflect the relative magnitude of the signals from the two targets. For convenience, some TOF pointers have been included at the top of the diagram.

A number of facts should be noted from the curves shown in Fig. 3. First, the peaks in the kinetic energy transforms do not correspond with the peaks in the TOF data. This is a product of the t^3 factor used in the transformation, [34]. Second, both kinetic energy distributions have maxima at rather low energies, < 0.2 eV, (with the CO₂ data being slightly more energetic), though the distributions extend to about 2 eV. This suggests that the dissociating states lie quite low within the manifold of possibilities and thus, the process defined by Equation (1) is a very definite possibility as a contributor to the observed signal in the case of CO₂.

It is of interest to compare our kinetic energy data with those obtained from photo-dissociation experiments though an exact comparison is not possible because the photon impact experiments make use of a single incident photon energy (wavelength) and thus access a single point on the particular repulsive surface in the Franck-Condon region. The electron impact studies on the other hand access all possible repulsive surfaces in the Franck-Condon region from threshold up to the nominal electron energy.

Neyer et al. [31] measured the energy distribution of O(¹D) fragments in a study of the photo-dissociation of N₂O using a ~200 nm YAG-pumped dye laser system and REMPI detection. They found a near Gaussian energy distribution peaked near 0.7 eV, with a high energy tail extending to beyond 1.5 eV and with a FWHM (full width-half maximum) of about 0.5 eV. They obtained quite good agreement with earlier REMPI experiments of Hanisco and Kummel [35], who measured the N₂ energy distribution and hence were able to deduce the distribution of the accompanying O fragment. These results were consistent with other photo-dissociation data of Felder et al. [36], and Springsteen et al. [37]. Based on the extensive calculations by Hopper [38] of the N₂O excited state manifold, these energies are very reasonable if dissociation occurs according to:



Neyer et al. [31], point out that dissociation of these states takes place via an avoided crossing with the $\text{C}^1\Pi$ state and because the molecule is severely bent, significant rotational excitation of the N_2 partner occurs. Since with electron impact we would be able to access these states at energies significantly below the 6 eV used in these photon impact experiments, it is very reasonable that our observed $\text{O}(^1\text{D})$ kinetic energies should extend to lower energies than in the photon work. Based on a comparison with the photon impact studies and also with the previous electron impact work on $\text{O}(^1\text{S})$ production from N_2O , by LeClair and McConkey [19], it is highly likely that the companion N_2 dissociation product is vibrationally excited as well.

Conclusions

A solid neon matrix has been used as a detector for metastable $\text{O}(^1\text{D})$ atoms in a study of the 100 eV electron impact dissociative excitation of N_2O and CO_2 targets. Measurements of fragment kinetic energies suggest likely dissociation channels. Comparison with photo-dissociation studies of these molecules suggests that significant vibrational excitation of the N_2 partner in the dissociation also occurs. Huestis and Slanger [39] note that, because of rapid quenching problems, the yield of $\text{O}(^1\text{D})$ atoms following photo-dissociation of CO_2 has never been measured. The present work suggests that this might be remedied using the Ne matrix detector technique.

Acknowledgements

The authors are grateful to the Canadian Natural Sciences and Engineering Research Council (NSERC), to the Canadian Foundation for Innovation (CFI), and to the Ontario Innovation Fund,

(OIF), for financial support for this work. The skilled assistance of the Physics electronic and mechanical workshop staff at the University of Windsor is gratefully acknowledged also.

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