Reaction and Electronic Excitation in Crossed-Beams Collisions of Low-Energy $O(^3P)$ Atoms with H_2O and CO_2

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(Received 23 July 1990)

Collisions of low-energy (5–20 eV), ground-state oxygen atoms with H_2O and CO_2 in a crossed-beams geometry lead to chemical reaction in the case of H_2O to produce OH ($A\,^2\Sigma^+ \rightarrow X\,^2\Pi$) emissions; and to inelastic electronic excitation in the case of CO_2 to produce the CO_2 ($\tilde{A}\,^1B_2 \rightarrow \tilde{X}\,^1A_1$) flame bands. Species identifications are made through known wavelengths and emission intensities in the range 300–400 nm. The measured difference in threshold energies for the two processes confirm the channels involved. These are the first measurements in this energy range of optical emissions through collisions of fast neutral species.

PACS numbers: 34.50.Lf, 34.50.Gb

We report herein results of the study of gas-phase reactions of low-energy (laboratory energy $E_{\text{lab}} = 5\text{–}20$ eV), ground-state $O(^3P)$ oxygen atoms with molecular targets. These reactions are interesting not only from a basic chemical dynamics point of view,[1,2] but clearly show that in environments where energetic atoms are expected—such as planetary and cometary ionospheres and magnetospheres,[3,4] combustion plasmas,[5] and the spacecraft environment[6,7]—entirely new reaction channels may be open which are normally endoergic at room temperature. The abundant optical emissions observed in the present work indicate that there is ready conversion of translational energy of a projectile to internal excitation, by either chemical reaction or inelastic collision. Results of these experiments are important in the development of predictive models and codes for understanding the different plasma environments. Previous work by Van Zyl and co-workers at higher energies (50 eV–2.5 keV) has shown that collisions of fast H atoms with N_2, O_2,[8] and Ne[9] produce excited H atoms. The present results are the first observations of reactive and inelastic collisions at energies near threshold, leading to molecular emissions in the products.

The atomic oxygen source used in these studies was described previously.[10] Briefly, $O^-(^2P)$ ions are formed via dissociative electron attachment to NO at 8-eV electron energy. No other negative ion, such as NO^-, can be formed under these conditions. Experiments are carried out in a uniform, high-intensity (6 T) solenoidal magnetic field. The O^- ions are accelerated to the desired final energy (10 eV, say), and separated from the faster electrons by a trochoidal field. The electrons are then photodetached to form $O(^3P)$ in a 100-pass mirror arrangement using all visible lines from a 20-W argon-ion laser. The undetached O^- ions are reflected by a biased mesh. The $O(^3P)$ atoms are directed towards the gas beam of H_2O or CO_2 formed by effusion from a small nozzle. The collision region is differentially pumped with respect to the O-source region. Base pressure in the collision region is 6.7×10^{-8} Pa (5×10^{-10} Torr), and typically 6.7×10^{-5} Pa (5×10^{-7} Torr) during operation.

Optical emissions from the target region in the wavelength range 300–850 nm are focused onto the entrance plane of a fast $f/3.5$ double-grating monochromator capable of attenuating by a factor of $>10^9$ the strong laser lines at 500 nm from the spectral range below 400 and above 600 nm. Calibration of the spectrometer resolution, and wavelength scale in the range 300–850 nm to an accuracy of 0.1 nm, was effected with emission lines from He, Ne, and Ar capillary discharge lamps. An RCA GaAs:CsO phototube and fast, pulse-counting electronics were used, and spectra recorded by multichannel scaling. All emissions were found to be linear in target gas pressure and O-atom flux.

Collisions of $O(^3P)$ with H_2O.—This reaction is endoergic by 0.04 eV. At high temperatures, such as in flames and combustion chambers, the reaction is known to occur, and rate constants have been measured.[11,12] In the present work, photon emission was observed in the wavelength range 300–850 nm starting at an O-atom energy of $E_{\text{lab}} \sim 8$ eV. The near-UV portion of the emission in the range 300–400 nm is characterized here. The reaction channel observed in H_2O is

$$O(^3P)(E) + H_2O(\tilde{X}\,^1A_1) \rightarrow OH(A\,^2\Sigma^+, v') + OH(X\,^2\Pi, v'') . \quad (1)$$

The threshold center-of-mass (c.m.) energy E for this reaction is calculated to be 4.5 eV, or a laboratory energy E_{lab} of 8.6 eV. This threshold assumes emission wavelengths $\lambda \geq 300$ nm, and zero c.m. kinetic energy in the outgoing OH partners. The $OH(A\,^2\Sigma^+)$ state was identified by line positions and calculated intensities of prominent features in the $A \rightarrow X$ transition. To relate the known wavelengths and intensities of individual lines to the observed emission spectrum, the standard expression for a Gaussian slit-width convolution is used:

$$I(\lambda) = \sum_k i_k \exp[-(\lambda - \lambda_k)^2/a^2] , \qquad (2)$$

where $I(\lambda)$ is the observed emission intensity at wavelength λ, λ_k is the known line position of the emitting state k, i_k is the intensity of the line at position k, and a is the full width at $1/e$ maximum, related to the full width at half maximum (FWHM) $\Delta\lambda$ by $a^2 = (\Delta\lambda/2)^2/\ln 2$. The summation k is over all lines emitting in the observed wavelength range.

Comparisons between the convolution of Eq. (2) and the observed spectra are shown in Fig. 1. The strong feature at 310 nm was identified by convolution of the spectrometer slit width (4 nm, FWHM), with positions[13] and calculated emission intensities[14] of the 0′-0″, 1-1, and 2-2 bands in the $A \rightarrow X$ system. Similarly, the observed feature at 350 nm was described in terms of positions and calculated intensities of the 0-1, 1-2, and 2-3 bands, and the partial feature near 400 nm through the 0-2, 1-3, and 2-4 bands.

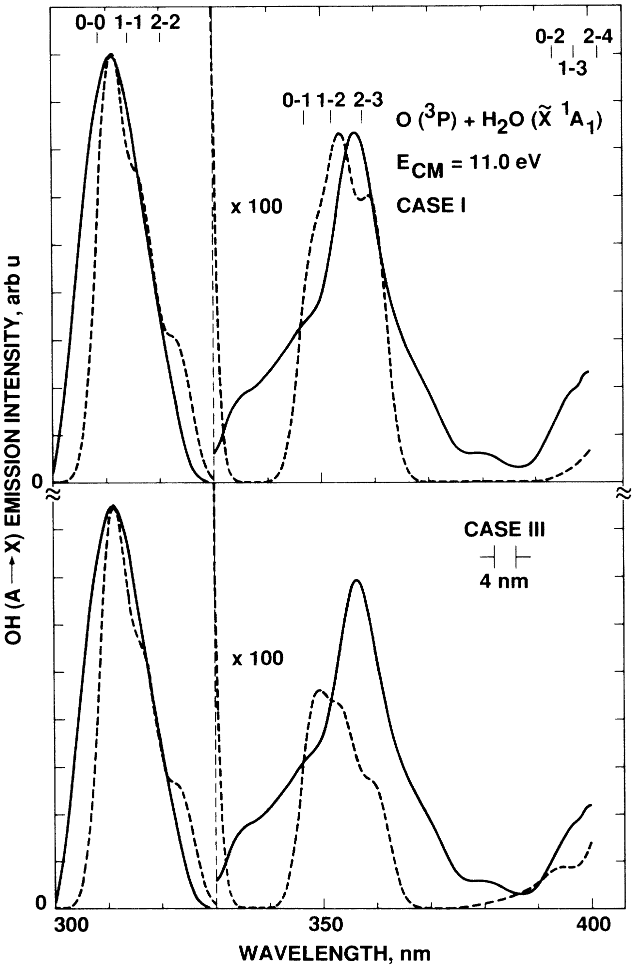

FIG. 1. Experimental (——) and calculated (---) emission spectra in the $A \rightarrow X$ transition of OH for the collision $O + H_2O$. Wavelengths are from Ref. 13 and emission intensities from Ref. 14 using two molecular-orbital calculations (cases I and III).

Also shown in Fig. 1 are convolution results using two separate basis-set calculations, so-called case I and case III.[14] In case I, internally consistent self-consistent-field (SCF) orbitals from the $X\,^2\Pi$ ground state were used in a configuration-interaction (CI) expansion of the excited-state wave function. In case III, the molecular orbitals chosen for the CI wave functions were obtained in an SCF calculation of the lowest $^2\Sigma^-$ state. Both cases were initially calculated for the rotational state $K=1$. However, there was a 2-nm difference between the measured and calculated positions of the bands. To compensate, a rotational value of $K=12$ was assigned to both the A and X states. Because of the difference in rotational B values of the states, this served to shift the calculated spectra 2 nm to the red. One sees clearly from Fig. 1 good agreement between present experiment and case I, $K=12$. Intuitively, one would expect that the energetic collisions between O and H_2O could result in the transfer of angular momenta to the nuclei in excess of thermal values, as has been measured in the reaction[15]

$$O(^1D_2) + H_2 \rightarrow OH(X\,^2\Pi, vK) + H(\text{oxygen-atom energy} \sim 0.3\text{ eV}) ,$$

and assumed in collisions resulting in pure vibrational excitation of H_2O.[16]

Collisions of $O(^3P)$ with CO_2.—This reaction was identified through the excitation channel

$$O(^3P)(E) + CO_2(\tilde{X}\,^1\Sigma_g^+) \rightarrow CO_2(\tilde{A}\,^1B_2) + O(^3P) , \qquad (3)$$

where the threshold center-of-mass collision energy is 4.1 eV ($E_{\text{lab}} = 5.6$ eV) for zero kinetic energy in the outgoing particles. Photon emission was observed throughout the wavelength range 300–850 nm. Presented in Fig. 2 are results in the range 300–400 nm.

To proceed with the identification, one notes that moderate vibrational and high-resolution rotational analyses have been reported by Gaydon[17] and Dixon,[18,19] respectively, on the so-called flame bands of CO_2. A photographic plate of this emission system is given in Ref. 20. These bands are produced by three-body recombination of O and CO into the bent $\tilde{A}\,^1B_2$ state of CO_2, followed by emission to the linear $\tilde{X}\,^1A_1$ ground state. A listing of the emission wave numbers and intensities was used.[17] A total of 102 individual transitions, together with a visual estimate by Gaydon of their intensity (on a scale of 1-5), was included in the summation of Eq. (2).

Comparison between present data and calculation is shown in Fig. 2. The agreement is quite satisfactory, and clearly shows that the observed emission spectrum is due to groupings of individual lines of the $^1B_2 \rightarrow {}^1A_1$

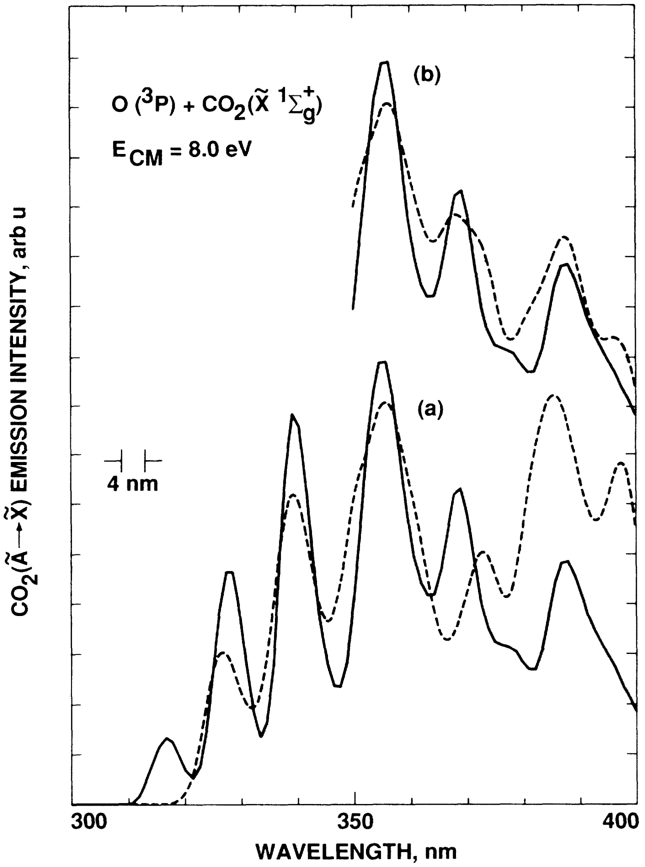

FIG. 2. (a) Experimental (——) and calculated (---) emission spectra in the $^1B_2 \rightarrow {}^1A_1$ transition of CO_2 for the collision $O+CO_2$. Wavelengths and intensities are from Ref. 17. (b) A fit where the visually estimated intensities (Ref. 17) contributing to the features at $\lambda > 360$ nm were adjusted.

transition in CO_2. No lines were listed for $\lambda < 325$ nm, so that correlation with the first feature at 317 nm was not possible. To gain a measure of the sensitivity of the results to changes in the visual intensity estimates, shown in Fig. 2(b) is the case wherein several listed intensity values[17] of "1" and "2" were increased to "2" and "3" for lines contributing to the peaks at wavelengths $\lambda > 360$ nm. These could be argued as reasonable changes, given the density versus log(exposure) characteristics of photographic plates, and the visual estimates involved.

As verification of these processes, it is interesting to point out that the difference in threshold energies between collisions in Eqs. (1) and (3) is calculated to be 3.0 eV. This difference was measured in the present work to be 3.3 ± 0.5 eV, consistent with the reaction channels involved.

It is worth speculating at this point about the mechanism(s) by which the collisions occur. In (1), the fast O atom collides with H_2O to capture an H atom and form an electronically excited- and ground-state OH. It is not possible at this time to determine with which electronic state the incident particle becomes associated. In (3) two channels are open: direct inelastic excitations of CO_2, or an exchange-type collision whereby the projectile displaces one of the target O atoms to form the bent $\tilde{A}\,^1B_2$ state. Isotopic labeling with ^{18}O will help determine which of the two channels is operant. Finally, analysis of the emissions herein was for the range 300–400 nm. Work is also underway to identify emissions observed in the range 600–850 nm for both interactions.

We thank S. R. Leone and C. Wittig for helpful discussions. This work was carried out at the Jet Propulsion Laboratory, Caltech, and was supported by the Geophysical Laboratory and Defense Advanced Research Projects Agency (DARPA) through agreement with NASA.

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