

ENERGY TRANSFER PROCESSES IN MONOCHROMATICALLY EXCITED $^{13}\text{C}^{16}\text{O}$ AND $^{12}\text{C}^{18}\text{O}$
 ($A^1\Pi v' = 13$) MOLECULES

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The narrow unreversed 123.58 nm resonance line of Kr excited exclusively the $A^1\Pi - X^1\Sigma^+$ (13,0) Q(13) transition of $^{13}\text{C}^{16}\text{O}$. A broader reversed 123.58 nm Kr resonance radiation excited the $A^1\Pi - X^1\Sigma^+$ (13,0) P(11), Q(13), and R(15) transitions of $^{13}\text{C}^{16}\text{O}$ and the P(10), Q(11), and R(14) transitions of $^{12}\text{C}^{18}\text{O}$.

The excited $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$ molecules fluoresce in the $A^1\Pi - X^1\Sigma^+$ (13, v'') resonance progression which was observed in the 200 to 310 nm spectral region (Fig. 1). Electronic quenching of the $A^1\Pi v' = 13$ state and rotational relaxation were studied as a function of the pressure of various molecules.

The $^{13}\text{C}^{16}\text{O}$ $A^1\Pi v' = 13$ state was quenched by: * $^{13}\text{C}^{16}\text{O}$ (198), $^{12}\text{C}^{18}\text{O}$ (38.0), $^{12}\text{C}^{16}\text{O}$ (57.1), CO_2 (119), O_2 (43), N_2 (78.5), H_2 (19.0), D_2 (29.3), He (<0.4), Ar (3.23), and Xe (114). The $^{12}\text{C}^{18}\text{O}$ $A^1\Pi v' = 13$ state was quenched by: * $^{12}\text{C}^{18}\text{O}$ (257) and $^{12}\text{C}^{16}\text{O}$ (28.0). The $^{13}\text{C}^{16}\text{O}$ $A^1\Pi v' = 13 J' = 13$ state was rotationally relaxed by: * He (3), $^{13}\text{C}^{16}\text{O}$ (16), and $^{12}\text{C}^{18}\text{O}$ (16).

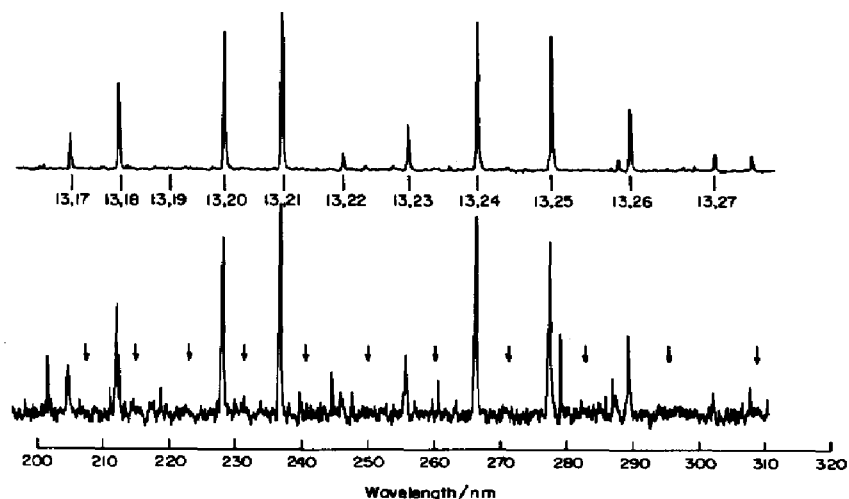
The quenching cross sections of the $A^1\Pi v' = 13$ state by the various molecules correlate with the availability of accessible electronic states and/or chemical reaction channels.

*The cross section, defined as $\sigma_q = k_q/c$, is given in A^2 in parenthesis.

The striking variation of the electronic quenching cross sections of the $A^1\Pi$ $v'=13$ state by the various isotopic CO molecules was attributed to fast energy transfer processes between the $A^1\Pi$ $v'=13$ state and a number of adjacent electronic states ($a^3\Pi$, $a'^3\Sigma^+$, $d^3\Delta_f$, $e^3\Sigma^-$, $I^1\Sigma^-$, $D^1\Delta$) which are known from spectroscopic measurements to perturb the $A^1\Pi$ state of CO¹. Similar variations in the quenching data of Melton et al^{2,3} on the $A^1\Pi$ $v'=9$ and $v'=14$ states of CO corroborate the above proposition.

References:

1. R. W. Field, B. G. Wicke, J. D. Simmons, and S. G. Tilford, *J. Mol. Spectrosc.* **44**, 383 (1972).
2. L. A. Melton and K.-C. Yin, *J. Chem. Phys.* **62**, 2860 (1975).
3. L. A. Melton and H.-T. Yao, *J. Chem. Phys.* **64**, 4689 (1976).



The $^{13}\text{C}^{16}\text{O}$ $A^1\Pi - X^1\Sigma^+$ ($13, v''$) resonance progression with 2.22 Torr $^{13}\text{C}^{16}\text{O}$ (upper trace) and with 61.4 Torr natural isotopic abundance CO (lower trace). The arrows indicate the same progression of $^{12}\text{C}^{16}\text{O}$, had it been excited.