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ELECTRONIC EXCITATION OF THE $A^1\Pi$ AND $b^3\Sigma^+$ STATES OF $^{12}C^{16}O$, $^{13}C^{16}O$ AND $^{12}C^{18}O$ BY $Kr(^3P_1)$ AND $Kr(^1P_1)$

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Krypton $^3P_1$ and $^1P_1$ atoms, formed by resonance absorption of 123.58 nm and 116.48 nm radiation by ground state Kr, sensitize the $A^1\Pi - X^1\Sigma^+$ and $b^3\Sigma^+ - a^3\Pi$ fluorescence of CO (Fig. 1).

The $Kr(^3P_1)$ state excited preferentially the $A^1\Pi$ $v' = 13$ state of $^{13}C^{16}O$ and $^{12}C^{18}O$ by a resonance energy transfer process. No such energy transfer process was observed between $Kr(^3P_1)$ and $^{12}C^{16}O$.

An examination of the energy level manifolds of the three isotopic molecules reveals that in the case of $^{13}C^{16}O$ and $^{12}C^{18}O$ there are several near resonance
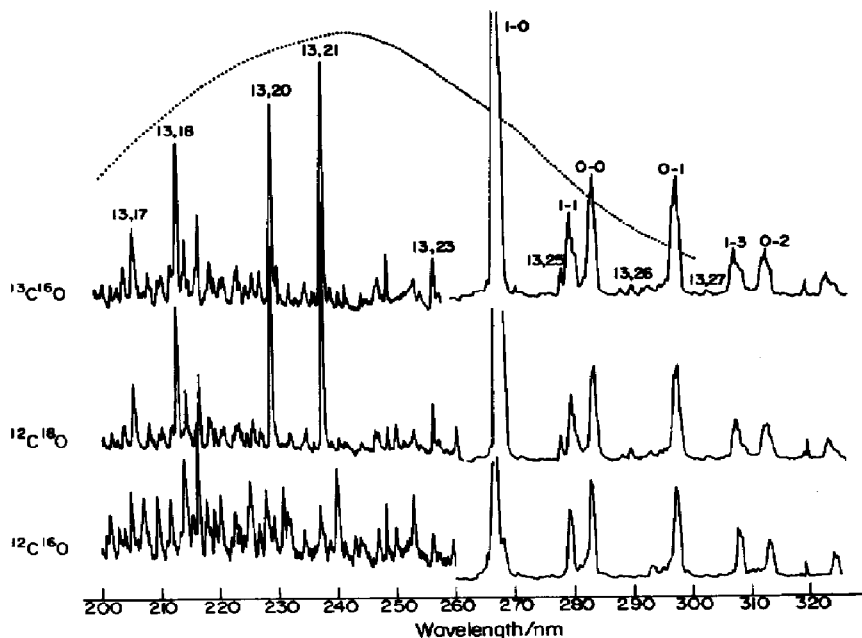
The $A^1\Pi - X^1\Sigma^+$ and $b^3\Sigma^+ - a^3\Pi$ fluorescence of $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$ sensitized by $Kr(^3P_1)$ and $Kr(^1P_1)$. The A-X transitions are indicated by v', v" and the b-a transitions by v'-v". The fluorescence intensity beyond 260 nm was attenuated by a factor of ten. The dotted line in the top spectrum indicates the monochromator-photomultiplier spectral sensitivity.

transitions, $\Delta E < 50$ cm^{-1}, which involve low $|\Delta J|$ changes and also originate from low rotational levels which are well populated at room temperature. By contrast, $^{12}C^{16}O$ can be excited with $Kr(^3P_1)$ in a resonance process with transitions involving low $|\Delta J|$ changes but originating from the sparsely populated high J levels, or with transitions originating from low J levels but involving high $|\Delta J|$ changes. Neither of the two processes are favoured according to the long range dipole-dipole energy transfer model[1], in agreement with the experiment.

The $Kr(^1P_1)$ state excites indiscriminately the $b^3\Sigma^+$ state of all three isotopic molecules. The population ratio of the two accessible vibrational levels of the $b^3\Sigma^+$ state, N(1)/N(0), was 0.17 for all three isotopic molecules. It is proposed that energy transfer in the latter case proceeds by a non-resonance mechanism due to the forbidden character of the $b^3\Sigma^+ - X^1\Sigma^+$ transition. The vibrational distribution of the $b^3\Sigma^+$ state and the lack of resonance behavior is indicative of strong interaction between the energy donor and the energy acceptor, similar to energy transfer reactions of rare gas and mercury metastables[2,3,4].

References

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