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THE OXYGEN AURORAL TRANSITION LASER SYSTEM
EXCITED BY COLLISIONAL AND PHOTOLYTIC ENERGY TRANSFER ^{*†}

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ABSTRACT

The properties of laser media involving the auroral transition of atomic oxygen and analogous systems are examined. A discussion of the atomic properties, collisional mechanisms, excitation processes, and collisionally induced radiative phenomena is given. We find that crossing phenomena play a particularly important role in governing the dynamics of the medium.

I Atomic Properties and Interactions

It is now clearly established that certain metastable atomic species which are open shell systems exhibiting the characteristics of a two electron spectrum have several properties that are unusually well suited for high power lasers.^{1,2} The states that appear most appropriate for energy storage are the $1S_0$ terms which correspond to the highest levels of np^2 and np^4 configurations (two electron or two hole systems, respectively). Aside from the order of the fine structure levels of the lowest $3P$ manifold, the energy level structures of these two configurations are identical. As an example, figure (1a) shows the terms of the oxygen atom relevant to our discussion. The three states ($3P$, $1D$, and $1S$) arising from recoupling of the electrons in the $2p^4$ configuration are shown in addition to other levels originating from excited configurations³ (i.e. $5S$, $3S$, $5P$, and $3P$). The corresponding data are illustrated in Figure (1b) and Figure (1c) for sulfur and selenium, respectively. At this point we will concentrate our discussion on the first three members of column VI (O, S, and Se) as these appear to be the most favorable candidate systems.

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Figure 1. Partial energy level diagram characteristic of column VI atoms illustrating the term values pertaining to the np^4 configuration as well as selected excited states arising from excited configurations. The particular term values of O, S, and Se are shown in (a), (b), and (c) respectively.

The radiative and collisional characteristics of these metastable systems are remarkable. We begin with the free system radiative properties which are compiled in Table I with the assumption that the optical cross sections listed correspond to regular broadened transitions at a temperature of 300°K . Note that for selenium, hyperfine effects and the normal isotopic abundance of selenium isotopes, provides

Table I

ATOMIC PROPERTIES

Line	Transition	Wavelength (Å)	Lifetime (sec)	Cross Section (cm^2)
1	$1s_0 \rightarrow 1D_2$	5577	~ 0.7	9×10^{-20}
2	$1s_0 \rightarrow 3P_1$	2958	~ 15	5.2×10^{-22}
3	$1s_0 \rightarrow 1D_2$	7726	~ 0.56	4.5×10^{-19}
4	$1s_0 \rightarrow 3P_1$	4589	~ 2.9	3×10^{-20}
5	$1s_0 \rightarrow 1D_2$	7768	~ 0.43	4.8×10^{-19} (9.7×10^{-19})*
6	$1s_0 \rightarrow 3P_1$	4887	~ 0.13	4.0×10^{-19} (8×10^{-19})*

* Calculated single isotope rather than normal isotopic abundance.

an additional mechanism for the variation of the optical cross section. The $^1S_0 - ^1D_2$ transition arises from the electric quadrupole (E2) transition moment while the $^1S_0 - ^3P_1$ is a magnetic dipole transition (M1) which violates the spin rule⁴. We observe that for selenium the magnetic transition is stronger than the electric quadrupole transition, a fact which serves to contrast with the lighter two species.

The collisional behavior of the 1S_0 term of these atoms is exceptional. Generally, collisions can transfer energy into kinetic energy of motion, internal excitation, or radiation. In terms of the 1S_0 state, we desire low cross sections for the former two inelastic processes as these represent nonradiative losses of the stored energy. We will see later that collisions can have a dramatic and desirable influence on the radiative properties of the medium and allow a convenient mechanism for adjusting the coupling of stored energy to the electromagnetic field. Table II and Table III illustrate, respectively, the quenching rate data for oxygen and sulfur

Table II
DEACTIVATION RATES OF ATOMIC OXYGEN METASTABLES*

Collision Partner	$O(^1S_0)$	$O(^1D_2)$
N_2	$< 5 \times 10^{-17}$	5.5×10^{-11}
N_2O	1.5×10^{-11}	2.2×10^{-10}
NO	4×10^{-10}	2.1×10^{-10}
$O(^3P)$	7.5×10^{-12}	--
CO_2	4×10^{-13}	2.2×10^{-10}
CO	9.4×10^{-14}	7.5×10^{-11}
Ar	5.2×10^{-18}	10^{-12}
Xe	6.7×10^{-15}	10^{-10}

* Rates given in $cm^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for 300°K. For further details and references see the material in Ref. (2). The majority of these rates are reviewed in R. J. Donovan and D. Husain, Chem. Rev. 70, 489 (1970).

1S_0 and 1D_2 states in collision with a variety of partners. Data for the corresponding states of selenium do not currently exist, although we anticipate roughly similar behavior. Two basic facts are apparent: the 1S_0 states relax slowly in collisions with several systems while the corresponding 1D_2 states quench orders of magnitude more rapidly. We will see that this difference in behavior is produced by the presence of an available surface crossing in the 1D_2 reaction channel and the absence of such a crossing mechanism in the 1S_0 case.

Table III

DEACTIVATION RATES FOR ATOMIC SULFUR METASTABLES*

Collision Partner	$S(^1S_0)$	$S(^1D_2)$
OCS	4×10^{-13}	8×10^{-11}
CO	$< 3.5 \times 10^{-16}$	2.2×10^{-11}
CO ₂	$< 6 \times 10^{-17}$	2.6×10^{-11}
CS ₂	8×10^{-10}	--
Ar	$< 3.5 \times 10^{-17}$	2×10^{-12}

* Rates given in $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ for 300°K . Data concerning the sulfur rates are contained in R. J. Donovan, Trans. Faraday Soc. 65, 1419 (1969); R. J. Donovan, L. J. Kirsch, and D. Husain, Trans. Faraday Soc. 66, 774 (1970); O. J. Dunn, S. V. Filseth, and R. A. Young, J. Chem. Phys. 59, 2892 (1973).

At high excited particle densities ($\sim 10^{17} \text{ cm}^{-3}$) inelastic collisions between two excited species will impose a fundamental limitation on the maximum achievable stored energy density. For example, a mechanism of this nature is known to be a limiting process in the rare gas excimer systems⁵. In this case, we require a low probability for inelastic scattering in an encounter between two excited 1S_0 systems. Specifically, we would like the dominant channel to be elastic such as that given by the following reaction involving two oxygen atoms.

Such collisions redistribute the kinetic energy of relative motion, but leave internal motions unaffected.

Dominance of the elastic channel for the scattering of two electronically excited atoms establishes requirements on the nature of the interatomic potential and on the relationship of that potential to other curves of the diatomic system. We now examine these characteristics for the case of O_2 . S_2 and Se_2 will be similar to O_2 as will the heteronuclear systems such as SSe except for the absence of gerade and ungerade symmetry. We expect the elastic process given by reaction (1) to dominate the scattering under circumstances for which no mechanism exists to (a) convert internal energy to kinetic energy of relative motion and (b) to resonantly excite another mode of internal excitation. An example of the former is the reaction

while the process

is characteristic of the latter. For an analysis of these reactions we refer to the potential energy curves available for O_2 shown in Figure (2) as derived from the

Figure 2. Energy levels of the oxygen molecule as compiled from the literature.^{6,7}

appropriate sources.^{6,7} We note immediately that the $1\Sigma_g^+$ curve arising from the $O(^1S) + O(^1S)$ interaction is of strongly repulsive character, and therefore, does not cross or even significantly approach any other curve of the diatomic system for kinetic energies below 2 electron-volts. Since normal thermal velocities correspond to approximately 0.025 electron-volts, the repulsive nature of this curve prevents the atoms from entering a region where transitions to other states of the O_2 system could occur. For example, no crossing with the ionic $O_2^+(X^2\Pi_g)$ curve is available at thermal energies, a fact which prevents reaction (3) from having an appreciable amplitude. In this $1\Sigma_g^+$ state the system is isolated from other channels and elastic scattering is expected to dominate.

Quite the opposite behavior is characteristic of the 1D_2 states, a fact which is strongly suggested by its relatively rapid quenching. The reaction

has been considered extensively in the literature.^{8,9} In this case, the presence of a strong attraction enables crossing with other potentials rising from below.

This crossing now provides an efficient mechanism for the conversion of electronic energy into the energy of nuclear motions. For N_2 this energy can appear as both vibration and translation. Experimental data verifying this conclusion have been obtained for the reaction¹⁰

where $CO^\dagger(X)$ denotes a vibrationally excited system.

II Collisionally Stimulated Radiation

Under ambient conditions consisting of a high pressure of rare gas (e.g. 25 atmospheres of krypton) the radiative properties of the excited system are grossly changed from those of the free atom. These changes are manifestations of the collisional influence on the radiative properties of the free atoms. Both the radiative rate and the bandwidth of the fluorescence are substantially modified. The upper spectrum in Figure (3) illustrates the spectrum of the fluorescence observed in an

Figure 3. The spectra (densitometer traces) of fluorescence and stimulated emission from KrO observed in a mixture of 5 torr O_2 and 25 atmospheres of Kr . The upper spectrum illustrates the observed fluorescence while the lower shows the stimulated spectrum.

electron beam excited mixture consisting of 5 torr O_2 and 25 atmospheres Kr. A structured peak slightly displaced from the position of the atomic line and a long blue wing are observed. For comparison, the lower spectrum in Figure (3) shows the spectrum of the stimulated emission observed from this same mixture.

The emitting species is the quasi-molecule KrO^+ and can be regarded as a manifestation of the process

Such collisionally induced emission is generally characteristic of these oxygen metastables for collisions with closed shell systems of both atomic and molecular varieties¹¹ (e.g. Ar and N_2). The heavier atoms sulfur and selenium will exhibit analogous behavior. It is important to note that for the quenching of $O(^1S)$ by the rare gases induced radiation is the dominant channel and accounts for the total quenching rate.¹² The collision dynamics discussed earlier prevent a contribution from other inelastic channels, and thus, allow the radiative mechanisms to dominate the inelastic scattering. Under the circumstances the net rate of emission via the molecular process is then directly proportional to the collision rate, or equivalently the density. The linewidth is determined by the relationship between the induced emission probability and the associated level shifts and is, hence, independent of density. The stimulated emission cross section, which is proportional to the ratio of these two quantities, then scales as the density of the medium. We state finally that considerable variation in this parameter is achievable, since the collision induced rates for the rare gases cover several orders of magnitude.¹²

III Kinetic Processes

The desired 1S_0 can be excited by both radiative, collisional, and presumably, combined radiative/collision processes. Radiative mechanisms such as

and

are known to exhibit high quantum yields (> 80%) and provide an attractive means for excitation, since the quanta required may be efficiently generated from the rare gas continua.¹³ The Ar_2 continuum is an excellent match for the N_2O spectrum while the Kr_2 continuum has a similarly superb overlap with the corresponding OCS absorption.¹⁴ The radiative processes for the oxygen system are thoroughly examined in Ref. (2). A most fortuitous match also exists for the Xe_2 continuum at $\sim 1715 \text{ \AA}$

with the strong band¹⁵ in OCS_e which is currently believed to lead to photolytic production of Se(¹S₀).

Several collisional mechanisms exist which are capable of producing the desired excited atoms². We list below a number of mechanisms which can play a role for oxygen, a case for which there is considerable data stemming from atmospheric studies.¹⁶

The cross section given theoretically for process (9) is $\sim 3 \times 10^{-18} \text{ cm}^2$ at 9 eV while the competing reaction generating O(¹D) has a value $\sim 3 \times 10^{-17} \text{ cm}^2$ at the same energy.¹⁷ For oxygen bearing impurities in high pressure rare gases excited by relativistic electron beams another mechanism has been proposed.¹⁸ It is under these circumstances that stimulated emission¹⁹ has been observed from ArO⁺, KrO⁺, and XeO⁺. An example of the process suggested by Huestis is

which is similar mechanistically to that proposed for an atomic metastable (Ar⁺) reaction by Golde and Thrush.²⁰ The entrance channel switches to the attractive ionic curve which, on account of its deep binding, crosses the exit channel and thus provides a pathway for process (15). Crossings again play a dominant role.

IV Concluding Remarks

We conclude by observing that the column VI materials O, S, and Se are attractive candidates for high energy laser systems, a finding which is based on both the free system and collisional properties of these atoms. In this discussion the behavior of surface crossings emerged in a central position for both excitation and quenching mechanisms. Indeed, collisions were seen in two complementary roles, governing the channeling of energy flow and in influencing the radiative properties of the medium.

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