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Production and properties of S(^1S) in liquid argon (88°K) and nitrogen (77°K)

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Photodissociation of OCS to produce S(^1S) has been observed in both liquid argon and liquid nitrogen over the wavelength range 144 to 161 nm. Over this wavelength range, the quantum yields are within a factor of 2 of those previously measured in the gas phase. Spectra of the emissions have been measured. The emissions have radiative lifetimes of (39 ± 2) μsec in liquid argon and (50 ± 3) μsec in liquid nitrogen. Evidence is presented that S(^1S) exists mainly as bound molecules in these media and that the lifetimes measured are those for the bound $2\,^1\Sigma^+ - 1\,^1\Sigma^+$ transitions. In these media the quenching of the emission by OCS has a rate coefficient of $(4\pm1)\times10^{-14}$ cm^3 molecule^{-1} sec^{-1}.

INTRODUCTION

Motivated by the laser fusion program, much work has been done on the photolytic production and properties of the ^1S states of O, S, and Se. In the case of S(^1S), efficient production from OCS was demonstrated[1] from 142 to 160 nm—a range which encompasses both the Kr_2 emission at 147 nm and the F_2 emission at 158 nm as potential photolytic sources in a high power laser amplifier. The collision-induced emission of S(^1S) has been studied in this laboratory[2–4] and the quenching of S(^1S) has been the subject of several earlier studies.[5–7] All this work has been confined to the gas phase.

Work in the solid phase has been confined to two studies[8,9] in which production of S(^1S) was demonstrated at 147 nm by observation of its matrix-induced emission. No lifetime information was obtained. In this laboratory studies of OCS is liquid argon under both *e*-beam and H_2 laser (161 nm) irradiation[10] showed S(^1S) production. With the H_2 laser, the radiative lifetime of S(^1S) in liquid argon was measured as (35 ± 10) μsec. For the *e*-beam pumping experiment, (58 ± 9) μsec was obtained. Furthermore, a value of $(3.5\pm0.9)\times10^{-13}$ cm^3 molecule^{-1} sec^{-1} was obtained for the quenching of S(^1S) by OCS in liquid argon. We have continued to study photolytic production and properties of S(^1S) in liquid argon using wavelengths from 144 to 161 nm. The results are a substantial improvement on those obtained earlier.

EXPERIMENTAL

The apparatus and techniques are as described previously.[11] In addition to the Ar and N_2 used previously, the OCS was used as a 10.8% mixture in prepurified argon. It was added to the system through a dry ice/acetone trap. Mixtures with argon and nitrogen were made up in a 30 liter volume in which turbulence introduced by the addition of the major gas was used to mix the contents. Mixtures containing from 0.1 to 2 ppm of OCS in two atmospheres of argon or nitrogen were liquified as previously.[11] Most of the measurements were made at 158 and 161 nm where the photolysis flux incident on the sample was $\approx 10^9$ sec^{-1} (compared to $\approx 10^8$ sec^{-1} at 144 nm). Even with 10^9 sec^{-1} incident on the sample negligible decomposition occurred over the time scale of the experiments. Hence quenching by photolytically produced impurities was not important. This was further confirmed by several measurements on each sample to ascertain that the decay rate did not change with irradiation time.

For these experiments, a Wratten 89B filter—EMI 9558QAM photomultiplier was used to view the emission in the vicinity of the $^1S-^1D$ transition at 772.7 nm. The intensity-time profiles, following pulsed excitation, were recorded with a MCA as described previously.[11]

RESULTS AND DISCUSSION

The spectral nature of the emissions, in both liquid argon and liquid nitrogen, is shown in Fig. 1. As with O(^1S) in these same media,[11] the $^1S_0\rightarrow{}^1D_2$ atomic transition (at 772.7 nm) appears as a predominantly red degraded band which differs from the predominantly blue degraded emission found in the gas phase.[3] We also see emission in the vicinity of the atomic transition at 459 nm [$^1S_0\rightarrow{}^3P_1$] in both liquids with approximately 0.005 the intensity of the long wavelength transition. No structure is apparent in the 459 nm feature. It does, however, exhibit a blue shift in liquid nitrogen (as does the long wavelength transition) relative to the position of the atomic line. No such shift is seen in liquid argon.

Measurements of the S(^1S) emission decay were made over the wavelength range 144 to 161 nm. In this region, with the experimental error (± 20%), the absorption cross section of OCS was not changed by dissolving in the liquid argon or nitrogen. A typical decay, using 158 nm excitation and liquid N_2 at 77 °K as the solvent, is shown in Fig. 2. The decay rates versus OCS concentration, for measurements in both liquid argon and nitrogen, are shown in Fig. 3.

Measurements of relative quantum yields for S(^1S) production over the range 144 to 161 nm, made in a similar way to the previous gas phase measurements,[1] established that the relative quantum yield versus wavelength curve had a similar shape to that measured in the gas phase. Furthermore, comparison with gas phase signals at 161 nm established that the absolute yields were within a factor of two of those measured in the gas phase. It appears, therefore, that these dense media do not substantially affect the photolytic yield of S(^1S) atoms.

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The intercepts of Fig. 2 give (39 ± 2) μsec for the radiative lifetime of $S(^1S)$ in liquid argon and (50 ± 3) μsec for the radiative lifetime of $S(^1S)$ in liquid nitrogen. The former value is in agreement with, but considerably more precise than the (35 ± 10) μsec obtained previously[10] in this laboratory for H_2 laser (161 nm) excitation but considerably smaller than the (58 ± 9) μsec obtained with *e*-beam excitation. Both the previous measurements were affected by rapid depletion of the OCS and by long-lived emission of $S_2(B \rightarrow X)$ radiation thought to arise from sulfur atom recombination.

As in our previous study[11] of $O(^1S)$ in liquid argon, we require additional information to resolve the measured lifetime into components arising for bound $(2\,^1\Sigma^+)$ molecules and from free $S(^1S)$ atoms (which produce emission from the repulsive wall of the $2\,^1\Sigma^+$ potential up to $\sim kT$ above the dissociation limit). Some guidance is provided by consideration of the values of the rate coefficient for collision-induced emission by argon at 296 and 232 °K determined in our previous work.[4] The values obtained were $(4.2 \pm 0.3) \times 10^{-18}$ and $(4.8 \pm 0.3) \times 10^{-18}$ $cm^3\,molecule^{-1}\,sec^{-1}$ at 296 and 232 °K respectively, with the slight increase at the lowest temperature arising from bound emission. With further cooling, based on consideration of the analogous $O(^1S)$–Ar system,[12] it is expected that the contribution from free emission will fall slowly but will be more than compensated by the increasing contribution from bound molecules. Hence a value of 5×10^{-18} $cm^3\,molecule^{-1}\,sec^{-1}$ is expected to be a lower limit on the collision-induced emission rate coefficient at 88 °K (the temperature of liquid argon). Using this value, then a radiative lifetime of ~ 10 μsec can be calculated for liquid argon density $(2.11 \times 10^{22}$ $cm^{-3})$. This is sufficiently smaller than our measured value that a major fraction of the $S(^1S)$ must be bound in ArS molecules under these conditions.

A similar conclusion is reached by estimating the equilibrium coefficient for the process

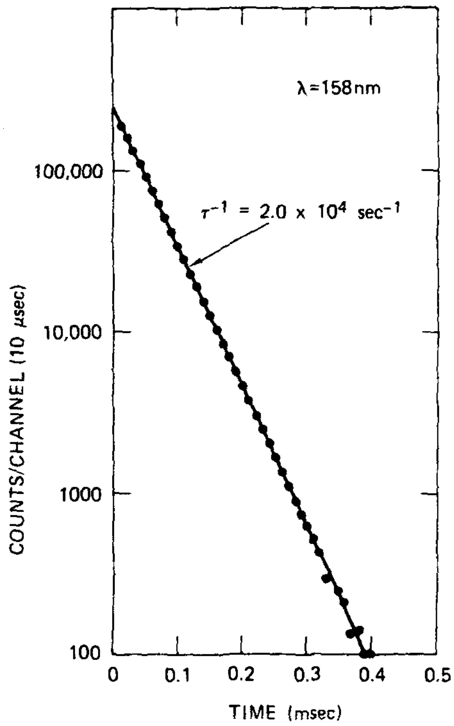

FIG. 2. Decay of $S(^1S)$ in liquid N_2 (77 °K) containing [OCS] $= 0.27 \times 10^{16}$ cm^{-3}. 3 min experiment at λ = 158 nm.

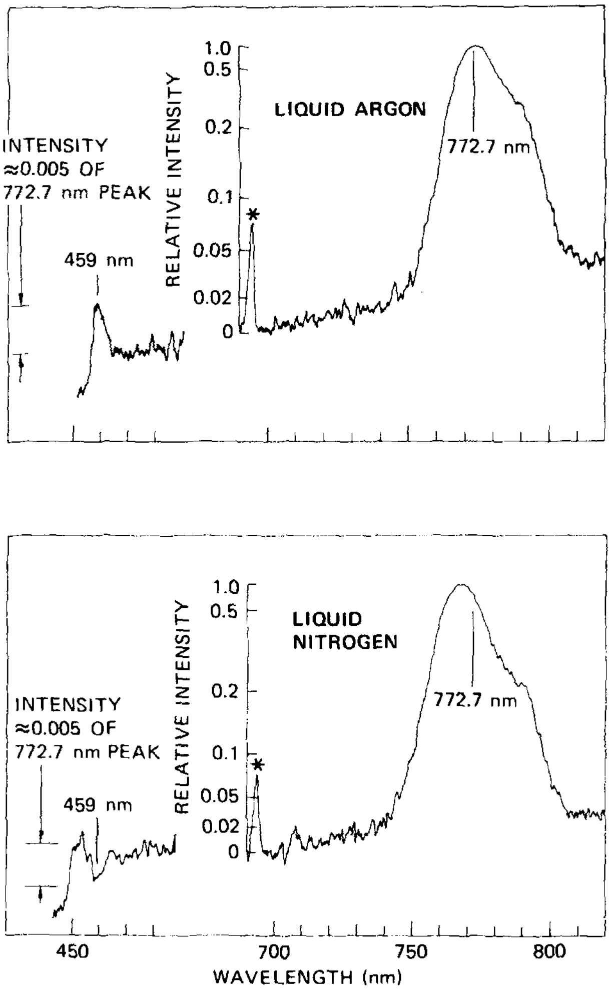

FIG. 1. Emissions following the production of $S(^1S)$ from OCS photodissociation in the wavelength region 140–161 nm, in both liquid argon (88 °K) and liquid nitrogen (77 °K). OCS = 0.35 ppm. Asterisks indicate scattered light from the H_2 photolysis lamp.

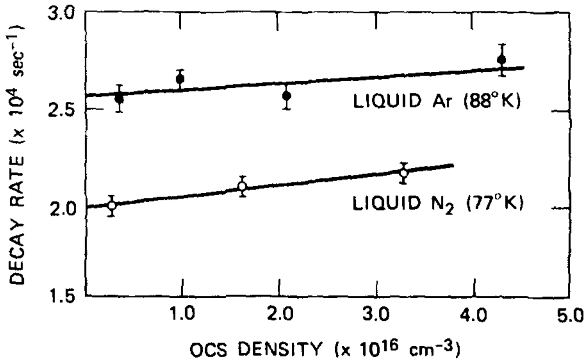

FIG. 3. Decay rate of $S(^1S)$ vs [OCS] in liquid argon (88 °K) and liquid N_2 (77 °K).

$$\mathrm{S}(^1S)+\mathrm{Ar}+\mathrm{Ar} \overset{K}{\rightleftarrows} \mathrm{ArS}(2\,^1\Sigma^+)+\mathrm{Ar}$$

for which

$$K=\left(\frac{h^2}{2\pi\mu kT}\right)^{3/3}[Q_{\mathrm{ArS}(2\,^1\Sigma^+)}/Q_{\mathrm{Ar}}Q_{\mathrm{S}(^1S)}]\exp(D/kT)$$

where Q represents the internal partition function and D is the dissociation energy of the ArS($2\,^1\Sigma^+$) potential. Using $D=98$ cm^{-1} (by approximating ArS to the corresponding rare gas ground state, Ar–Ar in this case),[13] an internuclear separation of 3.7 Å, and equating the vibrational partition function to unity we obtain K (at 88 °K) $=3.8\times10^{22}$ cm^3 molecule^{-1}. This gives ArS($2\,^1\Sigma^+$)/S(^1S) = 8 for Ar $=2.11\times10^{22}$ cm^{-3}. Although this is only an order of magnitude calculation, consistency with the above discussion of collision-induced emission reinforces the conclusion that S(^1S) in liquid argon exists mainly as bound ArS($2\,^1\Sigma^+$) molecules and that the radiative lifetime of ArS($2\,^1\Sigma^+$) is close to the measured value. A similar conclusion holds for the analogous molecule with N$_2$. As with our O(^1S)–liquid argon study,[11] we are unable to assess the effects of interacting with several neighboring argon atoms which must occur in the liquid medium.

The slopes of both lines in Fig. 2 give a rate coefficient of $(4\pm1)\times10^{-14}$ cm^3 molecule^{-1} sec^{-1} for the quenching of the emission by OCS in both liquid media. It must reflect a combination of quenching both the free and bound S(^1S). This is approximately an order of magnitude smaller than the $(4\pm2)\times10^{-13}$ cm^3 molecule^{-1} sec^{-1} determined for the quenching of S(^1S) by OCS at room temperature[7] after allowing for the effects of H$_2$S and CS$_2$ impurities. This reduced value may result from most of the S(^1S) being bound up as $2\,^1\Sigma^+$ molecules, and these molecules being less effectively quenched by OCS (or impurities it contains). It may also be a temperature dependence of the rate coefficient for the S(^1S)–OCS interaction as observed for O(^1S) quenching by N$_2$O.[11]

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