TWO-PHOTON DISSOCIATION OF CS_2 WITH A KrF LASER (λ = 248 nm)

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Summary

Two-photon excitation of CS_2 with the focused output of a KrF laser (248 nm) leads to the formation of CS radicals in the A $^1\Pi$ and X $^1\Sigma^+$ states. The vibrational distribution in the A $^1\Pi$ state is peaked around v' values of 3 or 4; however, the analysis is hindered by a strong laser-induced fluorescence signal from $CS(X\ ^1\Sigma^+)$. The results are discussed in the context of previous work on the single-photon excitation of CS_2 in the vacuum UV.

1. Introduction

The photochemistry of CS_2 has been quite extensively investigated and work up to 1977 was reviewed by Filseth [1]. More recently work on the vacuum UV photochemistry of CS_2 has been reviewed by Ashfold and co-workers [2, 3]. Since these reviews several papers involving laser excitation have appeared and are briefly outlined below.

Loree *et al.* [4] have used the tuned output from a frequency-narrowed ArF laser (about 193 nm) to separate ^{12}C–^{13}C and ^{32}S–^{34}S isotopes by photolysis of CS_2. Yang *et al.* [5] have made a detailed study of the photodissociation dynamics of CS_2 at 193 nm (ArF laser) but their results are partly at variance with those of Addison *et al.* [6] who were able to observe both states of the sulphur atom product directly (*i.e.* $S(3\ ^1D_2)$ and $S(3\ ^3P_J)$) using time-resolved atomic resonance fluorescence techniques. Butler *et al.* [7] have investigated the multiphoton excitation of CS_2 with an ArF laser and have observed extensive fluorescence from CS photofragments in the region 170 - 630 nm.

As CS_2 is a strong absorber at 193 nm the choice of an ArF laser for the work mentioned above is immediately understandable. The choice of a KrF laser (248 nm) for the present work is less obvious as CS_2 is transparent at this wavelength. However, we have recently shown [8] that two-photon

excitation of H_2O, D_2O and a number of other small molecules takes place when they are irradiated with the focused output of a KrF laser, although these molecules are also transparent at 248 nm. The immediate aim of our work in this area was to compare the photodissociation processes induced by two-photon absorption with those produced by single-photon absorption in the vacuum UV. The selection rules for two-photon absorption differ from those for single-photon absorption, particularly for molecules of high symmetry, and thus in principle two-photon excitation allows access to a range of previously unexplored excited states and hence potentially new photodissociation products.

2. Experimental details

The experimental arrangement used here for laser photolysis and for the observation of photofragment fluorescence has been described previously [8, 9]. Briefly it consists of a high power excimer laser (Lambda Physik EMG 500) capable of delivering (unfocused) about 10 MW cm^{-2} at 248 nm (KrF laser line); the pulse duration is about 20 ns. For the majority of experiments reported here the output of the laser was focused to an area of about 0.03 cm^2 in the observation region and thus the photon flux was typically of the order of 70 MW cm^{-2}.

A McKee–Pederson (MP 1018B) 0.5 m monochromator equipped with an EMI 9661B (S5) photomultiplier was used to observe the photofragment fluorescence. The output of the photomultiplier was fed to a Brookdeal 2415 linear gate and thence to a chart recorder.

3. Results

Excitation of CS_2 vapour (20 - 1.3 × 10^3 N m^{-2}) with the *unfocused* output from the KrF laser gave rise to a series of broad and weak fluorescence features in the 250 - 320 nm region. This emission was difficult to identify owing to its low intensity, but it lies in the region where fluorescence from CS(A $^1\Pi \rightarrow$ X $^1\Sigma^+$) is expected to occur (see below). We have not attempted to analyse this fluorescence further as it would require equipment of greater resolution and sensitivity than that available for the present work.

Focusing the laser into CS_2 vapour (20 - 1.3 × 10^3 N m^{-2}) produced very much stronger fluorescence signals as illustrated in Fig. 1. It is now possible positively to identify the fluorescence as arising from CS(A $^1\Pi$). The dominant emission is from the $v' = 4$ level of CS(A $^1\Pi$), but weaker fluorescence is observed from $v' = 3$ and $v' = 5$, with very weak fluorescence from the $v' = 2$ level. The relative fluorescence intensities and approximate level populations deduced using the known Franck–Condon factors [3] are given in Table 1.
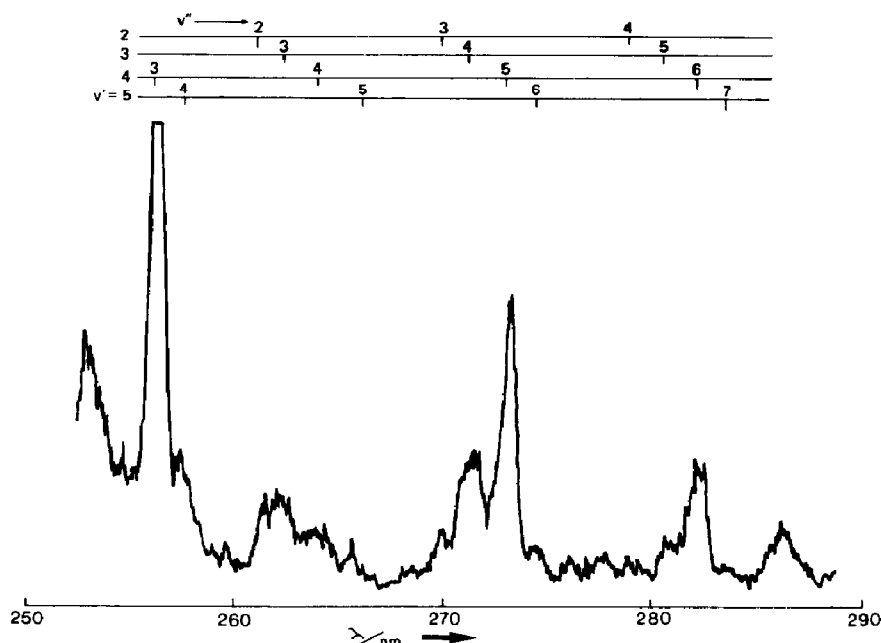
Fig. 1. CS(A $^1\Pi \to$ X $^1\Sigma^+$) fluorescence observed following two-photon excitation of CS_2 (λ = 248 nm): P_{CS_2} = 1.3 kN m^{-2}.

TABLE 1

The main fluorescence features, assigned to CS(A → X), and the approximate level populations observed after the two-photon excitation (λ = 248 nm) of CS_2

Observed wavelength (nm)	Assignment (v', v'')	Relative intensities	Relative v' populations
283.9	(5,7)	0.02	0.1
274.7	(5,6)	0.04	
257.7	(5,4)	0.10	
281.7	(4,6)	0.14	1
272.5	(4,5)	0.43	
263.6	(4,4)	0.06	
255.5	(4,3)	1.0	
280.7	(3,5)	0.04	0.3
271.0	(3,4)	0.14	
262.5	(3,3)	0.06	
269.7	(2,3)	0.07	0.2
261.0	(2,2)	0.09	

When pure CS_2 vapour was used the positions of the bands originating from v' = 4 appeared to be systematically displaced from their expected positions by about 0.3 - 0.7 nm; however, on adding CO_2 or N_2 (about 10 kN m^{-2}) the band positions were observed to shift to shorter wavelengths which then coincided with the expected positions of the band maxima. This

behaviour is consistent with the rotational relaxation of CS(A $^1\Pi$) by CO_2 and N_2. Ashfold *et al.* [3] have shown that these gases induce rotational relaxation more readily than electronic quenching, while for CS_2 the relative quenching rates are the opposite way round. Furthermore vibrational relaxation of CS(A $^1\Pi$) is much slower than electronic quenching for all these gases [3]. This behaviour operates to our advantage in the present work as it ensures that the observed vibration–rotation distribution in CS(A $^1\Pi$) is essentially the nascent distribution when pure CS_2 is used, even up to relatively high pressures (about 1.3 kN m^{-2}).

In addition to the CS(A $^1\Pi \rightarrow$ X $^1\Sigma^+$) fluorescence a few weaker features were also observed, notably at 286.4 and 292.3 nm, but could not be positively assigned. These may be related to bands observed by Butler *et al.* [7] following 193 nm (ArF laser) excitation, where again assignments could not be made for all the observed emissions.
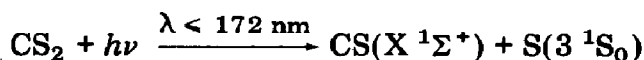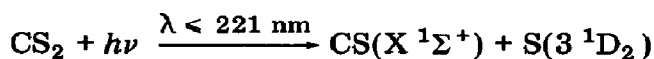

4. Discussion

The formation of CS radicals after laser excitation of CS_2 at 248 nm must involve the simultaneous absorption of two photons as CS_2 does not undergo single-photon absorption at this wavelength. This two-photon absorption process will populate highly excited Rydberg states in the region of the first ionization limit (124 nm $\equiv$ 80 645 cm^{-1}; the ionization potential of CS_2 is 81 346 cm^{-1}). These states will have *gerade* symmetry and will thus differ from those populated by single-photon absorption at 124 nm which will be of *ungerade* symmetry. We therefore expect the photofragments produced by two-photon excitation to differ from those produced by single-photon excitation. We note that the upper Rydberg states populated by two-photon excitation should be linear and have a geometry close to that of ground state CS_2^+, as is the case for single-photon excitation. The most likely states to be populated by two-photon excitation are the $^1\Pi_g$ ($ns\sigma_g$) Rydberg states.

The work of Ashfold *et al.* [3] on the single-photon dissociation of CS_2 at 124 nm showed that a wide distribution of vibrational levels, peaking at $v' = 0$, is produced in the CS(A $^1\Pi$) photofragment. In addition to the CS(A $^1\Pi \rightarrow$ X $^1\Sigma^+$) fluorescence, Ashfold *et al.* [3] also noted weak emission from CS(D $^3\Delta \rightarrow$ X $^1\Sigma^+$).
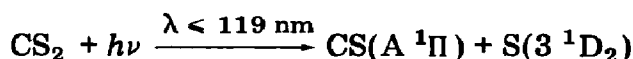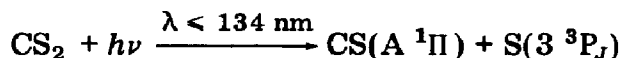
The results presented here for two-photon absorption are markedly different from those for single-photon excitation. The vibrational population of CS(A $^1\Pi$) reaches a maximum at $v' = 4$ and fluorescence from levels below $v' = 2$ is undetectable. A detailed discussion of level populations is not warranted at the present time as the limited resolution available did not allow a precise determination of the populations; however, it is clear that the $v' = 4$ level has a remarkably high population in comparison with neighbouring levels. We therefore looked for an alternative mechanism for populating this level and found that the (4,2) band of the CS(A $^1\Pi \leftarrow$ X $^1\Sigma^+$) system

overlaps with the KrF laser line. Thus CS radicals in the $X\,^1\Sigma^+$, $v'' = 2$ level can be pumped to the $A\,^1\Pi$, $v' = 4$ level, producing additional fluorescence in progressions originating from $v' = 4$. Further confirmation for this proposal comes from the fact that the laser line overlaps mainly with the high rotational levels of the (4,2) band which would account for the high rotational temperature and the observed shifts.

The origin of ground electronic state CS radicals is interesting as they must be formed within the time duration of the laser pulse (*i.e.* about 20 ns). This suggests that they are produced in a primary process as the radiative decay of $CS(A\,^1\Pi)$ is relatively slow ($\tau_R \approx 200$ ns) and collisional quenching will be inefficient on the time scale of the laser pulse, particularly at the lowest pressures used. We therefore propose that both $CS(A\,^1\Pi)$ and $CS(X\,^1\Sigma^+)$ are primary products of the two-photon dissociation of CS_2 at 248 nm. The formation of $CS(X\,^1\Sigma^+)$ could be accompanied by the formation of $S(3\,^1D_2)$ or $S(3\,^1S_0)$ as both are spin-allowed products. The energy requirements, given in terms of single-photon excitation, are as follows:

$$CS_2 + h\nu \xrightarrow{\lambda\,<\,221\ nm} CS(X\,^1\Sigma^+) + S(3\,^1D_2)$$

$$CS_2 + h\nu \xrightarrow{\lambda\,<\,172\ nm} CS(X\,^1\Sigma^+) + S(3\,^1S_0)$$

In contrast, the formation of $CS(A\,^1\Pi)$ at 124 nm must involve a spin-forbidden step as the only energetically allowed atomic product is $S(3\,^3P_J)$:

$$CS_2 + h\nu \xrightarrow{\lambda\,<\,134\ nm} CS(A\,^1\Pi) + S(3\,^3P_J)$$

$$CS_2 + h\nu \xrightarrow{\lambda\,<\,119\ nm} CS(A\,^1\Pi) + S(3\,^1D_2)$$

This may account for the low quantum yield (about 7%) of $CS(A\,^1\Pi)$ after single-photon excitation in the vacuum UV, although rapid intersystem crossing is known to occur after excitation at longer wavelengths [6], and this cannot be considered as a strong argument.

The work presented here is clearly of a preliminary nature and further work to establish more detailed information on the product state distribution after two-photon excitation of CS_2 at 248 nm is desirable. However, this will require more sophisticated equipment than that available to us at the present time.

In conclusion we note that these observations provide a cautionary note for the interpretation of photofragment fluorescence produced by excimer laser photolysis. The relatively broad output of these lasers ($\Delta\lambda \approx 1$ nm) can clearly lead to secondary excitation of photofragment species and this may dominate the observed emission spectra. Similar observations have been made by Fotakis [10] who has shown that secondary excitation of the SO radical, formed by photolysis of SO_2 with a KrF laser, produces strong fluorescence via the $SO(A\,^3\Pi \rightarrow X\,^3\Sigma^-)$ system. We note that the same type of

process is also known to occur with narrow band lasers. Wang and Davis [11] have shown that laser-induced fluorescence can be observed from OH radicals following two-photon excitation of water vapour at about 280 nm. In this case the excitation mechanism is readily identified, as laser-induced fluorescence only occurs when the laser line is tuned into coincidence with an absorption feature of OH.

Acknowledgment

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