

# Fluorescence lifetimes of rovibrational levels of the $B(0_u^+)$ state of $^{80}\text{Se}_2$

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## Abstract

Laser-induced fluorescence from  $^{80}\text{Se}_2(B(0_u^+), A(0_u^+))$  states has been examined and the fluorescence lifetimes of a number of unperturbed rovibrational levels of the B state measured. A collision-free lifetime of  $47 \pm 4$  ns is reported for the  $v = 3-6$ ,  $J < 82$  levels of the B state. The average of the square of the transition electric dipole moment for  $^{80}\text{Se}_2(B-X)$  has been deduced from experimental lifetimes and Franck-Condon factors to be  $|\mu_e|^2 = 8.06 \pm 0.66 \text{ D}^2$ .

## 1. Introduction

Homonuclear diatomic molecules made up of group VI atoms are potentially active materials for continuous-wave lasers [1,2]. The spectroscopic constants and potential energy curves for the low-energy states of the heavier elements  $\text{Se}_2$  and  $\text{Te}_2$  have been summarised [3]. Of particular concern to this Letter are the large spin-orbit coupling constants of these dimers. However, the dynamic information required for an understanding of a possible population inversion and laser action is scarce [4–11] and needs further consideration.

$^{80}\text{Se}_2$ , as expected for a Hund's case (c) molecule, exhibits two absorption band subsystems in the visible and UV regions, both components of the  $B^3\Sigma_u^- - X^3\Sigma_g^-$  system [12,3]. These subsystems

have been assigned to the  $B(0_u^+) - X(0_g^+)$  and  $B(1_u) - X(1_g)$  transitions; the last one is fairly weak and perturbed. The  $A(0_u^+) - X(0_g^+)$  transition was first observed by LIF in low-temperature Ar matrices [4,13,14]. More recently, Heaven et al. [5] obtained excitation spectra in gas phase samples, by analysing the fragments resulting from ablation of solid selenium by Nd:YAG laser pulses. Indeed, in the 377–400 nm region they assigned the 11–0 and 10–0 bands and suggested the first set of spectroscopic constants for the  $A(0_u^+)$  state.

The  $v = 0-15$  vibrational manifold of the  $B(0_u^+)$  state has numerous perturbations [12,15–17]. Some of them, identified in the  $v = 4-6$ , 13–15 levels, have been interpreted as arising from heterogeneous predissociation [12,18,19]. The perturbations observed in the  $v = 0-6$  levels are consistent with the existence of two  $1_u$  perturbing states, A and A' [17], assigned to the  $1_u$  components of the  $^3\Pi_u$  and  $^1\Pi_u$  electronic terms [3,17,20,21].

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In this work we report the fluorescence lifetimes of a number of rovibrational unperturbed levels [ $v = 3-6, J$ ] of the  $^{80}\text{Se}_2(\text{B}(0_u^+))$  electronic state as well as its average electric dipole moment.

## 2. Experimental

The experimental apparatus has been described recently [10,11] and only a brief summary will be given here. The main body of the cell consists of all-quartz cross-shaped tubes of different lengths ( $\approx 36 \times 12$  cm, 5 cm internal diameter), with two smaller diameter tubes attached in the centre the top and bottom. The latter is sealed and holds the solid  $^{80}\text{Se}$  sample (referred henceforth as 'finger'). The small tube is attached to the top ends in a suitable socket permitting the connection of the whole cell system to a vacuum manifold. Each of the four arms of the main body ends are sealed with optical windows. The sample cell was originally connected to a vacuum manifold for a thorough degassing of the quartz system and the sample at a pressure of  $10^{-7}$  Torr, and subsequently vacuum-sealed. The whole fluorescence cell was housed in a laboratory-made oven with two temperature controlled units, holding the 'finger' and the main body. Selenium, used as supplied by Harwell isotopes (80-Se), was evaporated in the 'finger' at  $T \leq 274^\circ\text{C}$  (estimated vapour pressure  $P = 70$  mTorr [22]) and heated to  $T \geq 500^\circ\text{C}$  in the main body. In these conditions the gaseous sample in the main body consists mainly of dimers ( $\text{Se}_2$ ) [23,24]. The temperatures of the two units of the oven were monitored with chromel–alumel thermocouples, and controlled within  $\pm 2^\circ\text{C}$ . Kinetic decays were found to have minor changes in the two days following the sealing of the cell.

The excitation system consists of a dye laser coupled to a Xe–Cl excimer laser (Lambda Physik FL3002E/EMG200E) working at a repetition rate of 10 Hz and yielding pulses of 22 ns fwhm. The spectral bandwidth of the dye laser was known to be  $0.04\text{ cm}^{-1}$ . Solutions of BBQ (Exciton) in dioxane were used as the active medium of the dye laser, giving laser emission energies of 1–2 mJ/pulse between 375 and 390 nm.

Fluorescent emission was detected with an RCA 1P28A phototube. Scattered light and oven emission

were removed by appropriate filters placed in front of the detector window. The phototube electrical signal was sent either (or simultaneously) to a boxcar integrator (Stanford Research SR250) attached to an  $X-t$  chart-recorder to record the LIF spectra or to a digital oscilloscope (Tektronix 2430A) to store the fluorescence decay traces.

## 3. Results

Excitation (LIF) spectra were recorded by collecting the total emission following laser excitation in the 380–390 nm region. Fluorescence decay signals of the main bands have bi-exponential profiles, with a fast decay ( $\tau_{\text{ap}} < 100$  ns) overlapped to a slow ( $\tau_{\text{ap}} = 800$  ns) and weaker one. Previous studies in this region reported a short lifetime emission ( $< 100$  ns) from the B state, and a long one (700 ns) from the A state [5,25,26]. Accordingly, spectra were recorded under two different conditions: (a) 1  $\mu\text{s}$  time delay between the laser pulse and boxcar integrator trigger, and boxcar observation through a 0.5  $\mu\text{s}$  gate width; (b) 50 ns time delay and gate width of 40 ns. Spectrum (a) should match that of the pure  $^{80}\text{Se}_2(\text{A-X})$  transition, while (b) is expected to be a mixture of both A–X and B–X transitions, dominated by the latter.

A first attempt at assignment of the spectrum was carried out by comparing the recorded spectrum and the simulated one generated from recent spectroscopic constants [27] for the  $\text{A}(0_u^+)$ ,  $\text{B}(0_u^+)$ ,  $\text{B}(1_u)$ ,  $\text{X}(0_u^+)$  and  $\text{X}(1_g)$  states. Unfortunately, no unambiguous rovibrational assignment emerges, due to the poor quality of the spectroscopic constants for the A state and to the perturbations present in the B state. Subsequently, the spectra were assigned by a sensible choice of bands of similar lifetimes and intensities. The procedure allowed the assignment of the rotational lines ( $J < 100$ ) of vibrational bands ( $v'-v'' = 5-2, 6-3, 4-2, 5-3$  and  $3-2$ ) of the electronic B–X transition. The vibrational band 12–1 of the  $^{80}\text{Se}_2(\text{A-X})$  transition was found to appear in the same spectral region, overlapping the B–X bands. The assignment has been used to label the states for which the lifetimes of a number of isolated lines of the B–X system have been characterised (Table 1). Lifetimes, as measured directly from fitting experi-

Table 1  
Fluorescence lifetimes of  $^{80}\text{Se}_2(\text{B}(0_u^+))$  ( $v, J$ ) rovibrational levels ( $v = 3-6$ )

$v$	$J$	$\tau$ (ns)
3	47	$46 \pm 2$
	55	$46 \pm 1$
	67	$46 \pm 1$
4	71	$48 \pm 3$
	73	$47 \pm 1$
	83	$49 \pm 1$
5	41	$47 \pm 2$
	53	$50 \pm 1$
	73	$48 \pm 2$
	75	$46 \pm 3$
	77	$46 \pm 1$
6	81	$47 \pm 1$
	27	$46 \pm 2$
	29	$49 \pm 1$
	31	$48 \pm 4$

mental data in a time interval of at least three times longer than those of the proper lifetimes, were all found to be close to 55 ns.

However, since the laser pulse width is sizeable compared to that of the apparent lifetimes, a deconvolution procedure was applied [28]. Real lifetimes are some 14% shorter and Table 1 shows the resulting lifetimes and estimated errors ( $1\sigma$ ) for isolated rovibrational ( $v, J, v = 3-6$ ) levels. Note that the fluorescence lifetimes are pressure independent and, therefore, collision free.

For the study of the deactivation kinetics of the  $\text{A}(0_u^+)$  state, three isolated bands from the stronger B–X system were carefully chosen. Unfortunately, their decays did not fit either a single exponential or even a sum of two exponentials and the analysis proceeded no further.

#### 4. Discussion

The vibrational bands of the  $\text{B}(0_u^+) - \text{X}(0_u^+)$  system assigned in this work involve perturbed vibrational levels of the B state ( $v = 3-6$ ). The perturbations are known to be  $J$  dependent and for the sake of the discussion the information available in the literature [12,17] is collected in Table 2. Comparing

the data from Tables 1 and 2, it becomes apparent that only fluorescence lifetimes of non-perturbed ( $v, J$ ) levels have been examined. As lifetimes are  $v$  and  $J$  independent, the value of  $\tau = 47 \pm 4$  ns is considered as the collision-free fluorescence lifetime for  $v = 3-6$  and  $J < 82$  levels of  $^{80}\text{Se}_2(\text{B}(0_u^+))$ . This value contrasts with that obtained by Heaven et al. of  $85 \pm 5$  ns resulting from a simultaneous double exponential fit of combined A and B state fluorescence, and is consistent with those of  $39 \pm 5$  ns reported by Stolyarov et al. for the  $v = 0, J = 129$  level [26], and  $58 \pm 6$  ns reported by Gouedard et al. of for  $v = 0, J = 105$  of the  $\text{B}(1_u)$  state [25]. It should be noted, however, that literature values refer to single rovibrational state lifetime measurements with no indication of  $v$  or  $J$  dependence.

As already mentioned, LIF decays of rovibrational  $\text{A}(0_u^+)$  bands are complex. A straightforward explanation of the behaviour would regard the emission as originating from both A and B states. However, decay fittings to two exponentials (one being  $\tau_B = 50$  ns) are unsatisfactory, thus ruling out the interpretation as band overlapping. Alternative explanations would require a more detailed kinetic study of the  $\text{A}(0_u^+)$  state.

The square of the electric dipole moment  $|\mu_c|^2$  is a more fundamental measure of the transition probability than the reciprocal radiative lifetime  $1/\tau_R$ . The spontaneous emission coefficient from an initial state  $v'$  to a final state  $v''$ ,  $A_{v',v''}$ , is related to the electric dipole moment by the expression

$$A_{v',v''} = \frac{1}{\tau_{v'}} = \frac{64\pi^4}{3h} \sum_{v''} |\mu_c|^2 q_{v',v''} v^3, \quad (1)$$

where  $q_{v',v''}$  is the Franck–Condon factor (FCF) for the  $v' - v''$  transition. Assuming a negligible variation

Table 2  
Perturbations found in the rovibrational levels ( $v = 3-6$ ) of the  $^{80}\text{Se}_2(\text{B}(0_u^+))$  state [12,17]

$v$	$J$ interval	Perturbations	Predissociation
3	$11 \leq J \leq 121$	$J = 17, 109, > 121$	
4	$3 \leq J \leq 107$	$J = 41, 53, > 107$	
5	$5 \leq J \leq 103$	$J = 65, > 103$	$J > 81$
6	$3 \leq J \leq 61$	$J = 41$	$J > 49$

Table 3

Values of  $\sum_{v''} q_{v',v''} \nu^3$  (see text) and electric dipole moments  $|\mu_e|^2$  for different vibrational levels ( $v'$ ) of the  $^{80}\text{Se}_2(\text{B-X})$  electronic transition

$v'$	$\tau(v')$ (ns)	$10^{-12} \sum_{v''} q_{v',v''} \nu^3$ ( $\text{cm}^{-3}$ )	$ \mu_e ^2$ ( $\text{D}^2$ )
3	$46 \pm 2$	8.4627	$8.19 \pm 0.37$
4	$48 \pm 3$	8.4014	$7.91 \pm 0.52$
5	$47 \pm 3$	8.3415	$8.13 \pm 0.56$
6	$48 \pm 4$	8.2831	$8.02 \pm 0.73$

of  $|\mu_e|^2$  with the  $r$  centroid  $\bar{r}$ , Eq. (1) can be approximated by

$$A_{v',v''} = \tau_{v'}^{-1} = \frac{64\pi^4}{3h} |\mu_e|^2 (\bar{\nu})^3, \quad (2)$$

where

$$(\bar{\nu})^3 = \sum_{v''} q_{v',v''} \nu^3.$$

In order to obtain the dipole moments,  $|\mu_e|^2$ , of the  $^{80}\text{Se}_2(\text{B-X})$  transition, Franck-Condon factors and  $(\bar{\nu})^3$  summations were computed for  $v'-v''$  vibrational transitions with  $v' \leq 20$  and  $v'' \leq 60$ , using Proser et al.'s parameters [27]. Values of  $(\bar{\nu})^3$ , shown in Table 3, have been calculated for  $v' = 3-6$  by summing over  $v''$  in the range  $0 \leq v'' \leq 50$ .  $|\mu_e|^2$  has been calculated from Eq. (2) and the lifetimes for  $v' = 3-6$  states shown in Table 1. The resulting dipole moment values for the vibrational levels studied are presented in Table 3 and have an insignificant dependence upon  $v$ . Therefore, the dipole moment of the  $^{80}\text{Se}_2(\text{B-X})$  transition is taken as the average of those of the vibrational transitions, i.e.  $|\mu_e|^2 = 8.05 \pm 0.66 \text{ D}^2$ . The values reported by Stolyarov et al. [26] refer to individual  $v'-v''$  transitions ( $v' = 1, v'' = 5-20$ ) and vary from 13.8 to 6.1  $\text{D}^2$ . The significant dependence on the  $r$  centroid implicit in these values suggests that the present results should be regarded as average values for each vibrational  $v'$  level.

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