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# A low- $n$ Rydberg state with vibrationally excited core assigned in the ZEKE–PFI spectrum of CS<sub>2</sub>

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Polyatomic molecules offer the possibility of studying the dependence of vibrational autoionization rate on the nature of the particular vibrational modes involved. For example, in NO<sub>2</sub>, as stressed by E. R. Grant, the symmetric stretching relaxes much faster than the bending motion. A particular feature observed in the ZEKE–PFI spectrum of CS<sub>2</sub> can be quoted as another example of the difficulty of relaxing the bending vibration in the ionic core of a triatomic molecule.

## 1. Experimental background and results

The ZEKE–PFI spectrum of jet-cooled CS<sub>2</sub> was recorded by Huang *et al.* (1997) using VUV laser excitation. After a typical delay of 3.8 μs the laser pulse was followed by a voltage pulse equal to 0.24 V cm<sup>-1</sup> and 1 μs duration. A reverse DC field of 0.08 V cm<sup>-1</sup> was used to sweep out prompt electrons.

The O<sub>0</sub><sup>0</sup> origin band of the spectrum, corresponding to ionization in the  $\tilde{X}^2\Pi_g$  ground state of CS<sub>2</sub><sup>+</sup>, presents two sub-bands, one for each of the two possible values of  $\Omega^+$  ( $\frac{1}{2}$  and  $\frac{3}{2}$ ), roughly separated by the spin-orbit coupling constant, 440 cm<sup>-1</sup>. A simulation of the band contours was made (Huang *et al.* 1997) which uses matrix diagonalization of the molecular energy in Hund's case (*e*) representation (Lefebvre-Brion 1990, 1995). The observed sub-band intensity ratio ( $^2\Pi_{3/2}/^2\Pi_{1/2} = 1.9 \pm 0.3$ ) could be accounted for by including rotational and spin-orbit autoionization and considering in the calculation a particular value of the principal quantum number, the meaning of which is discussed by Huang *et al.* (1997).

Superimposed on the  $\tilde{X}^2\Pi_{3/2}$  sub-band of the ZEKE–PFI spectrum, a quite strong peak (cf. figure 10*a* of Huang *et al.* (1997), where it is marked with an arrow) is observed at 81 274 cm<sup>-1</sup>. It happens that in the photoionization (PI) spectrum (Huang *et al.* 1997) is observed for the same wavenumber, the principal peak of the 17pσ Rydberg state with  $\tilde{X}^2\Pi_{1/2}$  ionic core. However, as it can be seen in the level scheme represented in figure 1, the upper level of the latter transition (vertical line on the left) is 12 cm<sup>-1</sup> below the  $\tilde{X}^2\Pi_{3/2}$  threshold. For the large Stark shifts corresponding to the PI spectra, the molecule can thus be autoionized in the ( $^2\Pi_{1/2}$ ) 17pσ state. But for the smaller Stark shifts typical of ZEKE–PFI spectra (from 1.6–1.7 cm<sup>-1</sup>, for the electric field values given above), the ( $^2\Pi_{1/2}$ ) 17pσ state can be only partially autoionized, for rotational energies exceeding 12 cm<sup>-1</sup> (i.e.  $J \geq 10$ , for a rotational constant  $B$  equal to about 0.1 cm<sup>-1</sup>).

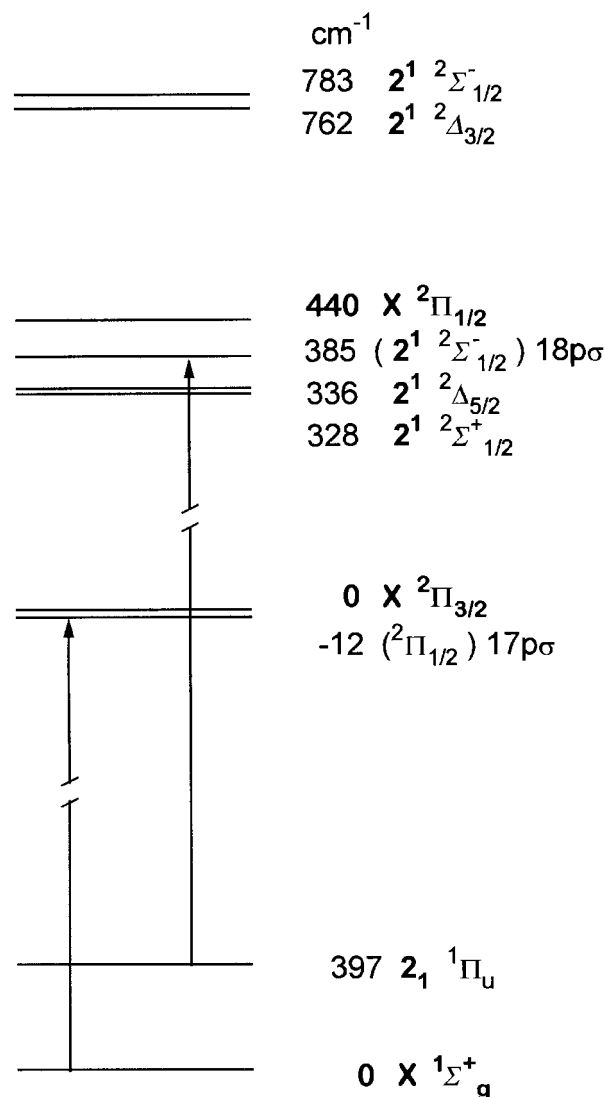


Figure 1. Vibrational levels in  $\text{CS}_2 \tilde{X}^1\Sigma_g^+$  and in  $\text{CS}_2^+ \tilde{X}^2\Pi_g$  states involved in the discussion of the assignment of the hot band transition shown on the right-hand side, which presents the same wavenumber as the cold-band transition represented on the left. Zero-rovibrational levels of the two states (separated by  $81\,286\text{ cm}^{-1}$ , cf. Huang *et al.* (1997)) are both used as origin of the wavenumbers given.

## 2. A hot band in the ZEKE-PFI spectrum involving a low- $n$ Rydberg state

Another assignment of the  $81\,274\text{ cm}^{-1}$  peak in the ZEKE-PFI spectrum is possible, which is more satisfying. In the same spectrum, which extends over  $1000\text{ cm}^{-1}$  (cf. figure 6 of Huang *et al.* (1997)), were assigned various vibronic bands allowing determination of the energies of the Renner-Teller split levels of the bending  $\nu_2$  ( $\pi_u$ ) vibration for  $v_2^+ = 1$  in the  $\tilde{X}^2\Pi_g$  of the  $\text{CS}_2^+$  ion. These are shown in figure 1, labelled as  $2^1$  with corresponding vibronic symmetries  $^2\Sigma_{1/2}^+$ ,  $^2\Delta_{5/2}$ ,  $^2\Delta_{3/2}$ ,  $^2\Sigma_{1/2}^-$ ,

in the order of increasing energies, which are also given in the figure (deduced from the  $2_1^1$  transitions observed by Huang *et al.* (1997), preferred here to the weaker  $2_0^1$  transitions also observed). These level positions were found to be in good agreement with the calculated results of the ion ground state by Brommer & Rosmus (1993). Now, considering the  $2^1$  ( $^2\Sigma_{1/2}^-$ ) limit with the same quantum defect value (0.4) as in the ( $^2\Pi_{1/2}$ )  $n\text{p}\sigma$  series, for  $n \geq 15$ , as observed in the PI spectrum by Huang *et al.* (1997) and in the VUV absorption spectrum by Cossart-Magos *et al.* (1997), one obtains, as indicated in figure 1, a  $18\text{p}\sigma$  state at  $385\text{ cm}^{-1}$  above the zero-level of  $\tilde{X}^2\Pi_{3/2}$ . The hot band transition represented by the vertical line on the right-hand side of figure 1, with a lower level  $2_1$  ( $^1\Pi_u$ ) at  $397\text{ cm}^{-1}$  from the zero-vibration level of the  $\text{CS}_2$   $\tilde{X}^1\Sigma_g^+$  state, and an upper level [ $2^1$  ( $^2\Sigma_{1/2}^-$ )]  $18\text{p}\sigma$ , is thus found at  $385-397 = -12\text{ cm}^{-1}$  (at the same frequency as ( $^2\Pi_{1/2}$ )  $17\text{p}\sigma \leftarrow \tilde{X}^1\Sigma_g^+$ ).

### 3. Conclusion

In conclusion, according to this hot band assignment, a Rydberg state with principal quantum number  $n$  as low as 18, can be observed in the experimental conditions of ZEKE-PFI spectroscopy, indicating that during the delay time of  $3.8\text{ }\mu\text{s}$ , relaxation of the vibrationally excited  $\text{CS}_2^+$  core is not yet completed.

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