Predissociation and Perturbation in the Selenium Molecule

It is known that the predissociation produced by the radiationless transition from an excited stable molecular state to an unstable one is responsible for the broadening of the absorption rotational lines and the increase in intensity of the perturbed bands. In the emission spectrum, the bands vanish in the region of perturbation. This usual case is well illustrated in the band system $B^3\Sigma_u^- - X^3\Sigma_g^-$ of S_2. In the progression $v'' = 0$, the absorption spectrum shows sharp band heads up to $v' = 9$, while the $v' = 10, 11 \ldots$ bands are very diffuse. At $v' = 10$ a strong intensity increase occurs. This predissociation corresponds to the case I(c) of Herzberg[1] due to an interaction between two excited states one of which is stable and the other of repulsive type. The crossing of these two potential energy curves occurs above the dissociation limit of the repulsive level. So far it is the only well-established case of this kind.

The foregoing appearance is not found in the similar transition $B\Sigma - X\Sigma$ of Se_2. In the progression $v'' = 0$, absorption bands are observed up to $v' = 22$, and are followed by a short-range continuous spectrum. The difference with S_2 is that in the small dispersion spectrum there is no apparent intensity increase. The perturbation seems so strong that the nearest diffuse bands have the aspect of a continuous background. The extrapolation of this progression gives for the short wave-length limit the value $\lambda_1 = 3200$ Å. On the other hand, the short wave-length limit of the continuous spectrum is $\lambda_2 = 2750$ Å. Thus, the continuous spectrum is actually made up from the broadened bands and a true short range continuum. The crossing point of the two interacting states is located near the dissociation limit of the stable state. Among the numerous sub-cases of predissociation of diatomic molecules discussed by Mulliken[2], only two may be considered here. In both cases the internuclear distance r_c of the crossing point is larger than r_e. If the perturbing state is a stable one, the case C+ occurs, where both potential curves have a common asymptote and both molecules originate from the same atoms $S(^3P) + S(^1D)$. In the second case the perturbing state is of repulsive type and originates from different atoms. In order to obtain more information concerning the broadening of the line, we photographed again the absorption spectrum near the limit of the progression $v'' = 0$. Fig. 1 shows a part of the spectrum taken in the region 3200 Å–3600 Å with a J Aco-Ebert spectrograph having a linear reciprocal dispersion of 0·6 per mm. The absorbing layer was 14·5 cm long and the pressure of selenium about 15 mm mercury. It is seen that the width of the rotational lines of the (18·0) band (Fig. 1, below) is about 3 times smaller than that of the (20·0) band (Fig. 1, above). In the same spectral region the rotation structure is simple and seems to correspond to a $^1\Sigma - ^1\Sigma$ transition. The rotational lines are well separated, and the effect of the perturbation is to broaden the lines in consequence of the decrease of the life-time of the excited state; but the broadened lines do not overlap in the (20·0) band. This is why there is no intensity increase of that band.

The following (21·0) band shows no rotational structure with the dispersion here used. Under small dispersion this band does not seem to be stronger than the (19·0) band. Therefore, we have to conclude that in the present case the decrease of the lifetime is associated with a greater width of the lines but not necessarily with a higher intensity of the perturbed band. It is known indeed that for a single line the total intensity absorbed is not sensitive to the shape of the line profile and basically depends on the product of the oscillator strength and the concentration of absorbing particles. The increase of the band intensity could only originate from the overlapping of the neighbouring lines.

To sum up, the perturbations in the $B\Sigma - X\Sigma$ transition are basically similar for the two molecules, Se_2 and S_2. In both cases diffuse bands are observed. Their number only varies. Contrary to what is observed in sulphur, selenium bands do not get sharp again when v' increases from the perturbation region, owing to the proximity of the dissociation limit. This results from the relative position of the potential curves of the stable excited state and the repulsive state, which cross each other near the dissociation limit of the stable molecule.

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[1] Herzberg, G., *Molecular Spectra and Molecular Structure*, 1, *Spectra of Diatomic Molecules*, second ed., 424 (D. Van Nostrand Co., New York, 1950).
[2] Mulliken, R. S., *J. Chem. Phys.*, 33, 247 (1960).

High-current Cathode for Electron Linear Accelerator

For many years, the bombarded tantalum cathode gun has acted as a reliable source of electrons for injection into demountable linear accelerator systems[1,2]. An important advantage of the pure metal cathode, such as tantalum or tungsten, is its high resistance to poisoning under adverse vacuum conditions which exist in linear accelerators during multipactor resonances, during high energy beam collision and clipping on inner surfaces, and, in particular, when the microwave structure is initially out-gassed by application of the radio-frequency power. Furthermore, after the cathode has cooled, the accelerator may repeatedly be opened to atmosphere, re-evacuated and the cathode returned to operating temperature without loss of emission and without additional precautions or special restrictions. On several occasions, vacuum systems containing pure metal cathodes at elevated temperatures have been inadvertently opened to atmosphere, and it has been possible to re-operate these guns satisfactorily.

Even with the assurance of an extremely clean system and a higher order of vacuum (10^{-8}–10^{-6} torr) as offered by the application of sputter-ion pumps[3] to high-power linear accelerators (the first such combination was a machine constructed for the Danish Atomic Energy Commission and operated in December 1959), preference remained for the bombarded tantalum cathode because it did not require bake-out procedures, isolating valves, or activation schedules as is the case, for example, with coated emitters.
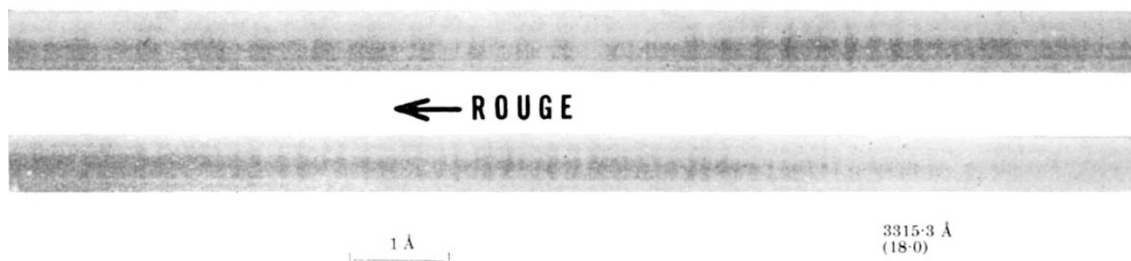
3274·0 Å
(20·0)

←ROUGE

1 Å

3315·3 Å
(18·0)

Fig. 1