ONSET OF INVERSION IN THE $^1\Sigma_{\bf g}^+$ \to $^3\Sigma_{\bf g}^-$ TRANSITION OF MOLECULAR SULPHUR FOLLOWING THE PHOTODISSOCIATION OF COS

V.S. Zuev, S.B. Kormer, L.D. Mikheev, M.V. Sinitsyn, I.I. Sobel'man, and G.I. Startsev

Submitted 6 July 1972

ZhETF Pis. Red. 16, No. 4, 222 - 224 (20 August 1972)

We report here observation of lasing at the wavelengths 1.0920 \pm 0.001, 1.0975 \pm 0.001, 1.100 \pm 0.001, and 1.1055 \pm 0.001 μ in the photodissociation of COS (see the figure). We identify this radiation with the electronic $^{1}\Sigma^{+}_{}$ \rightarrow $^{3}\Sigma^{-}_{}_{}$ transitions of the S2 molecule, which belong to the series v + 1 \rightarrow v.

It follows from the work of Gunning, Strausz, et al. [1] that the absorption of light by the COS molecule in the band with maximum at 2250 Å leads to photodissociation in accordance with the reaction

$$COS + h_{\nu}(\lambda_{mg,x} = 2250 \text{ Å}) \rightarrow CO + S$$
 (1)

and that sulfur atoms in the excited state $^1\text{D}_2$ are produced in at least 74% of the dissociations. The photodissociation (1) is accompanied by the chain of reactions

$$S(^{1}D_{2}) + COS \xrightarrow{K_{2}} CO(X^{1}\Sigma^{+}) + S_{2} (\sigma^{1}\Delta_{\sigma} \text{ and perhaps } b^{1}\Sigma_{\sigma}),$$
 (2)

$$S(^{1}D_{2}) + COS \stackrel{k_{3}}{\rightarrow} COS^{*} + S(^{3}P_{i}),$$
 (3)

$$S(^{3}P_{i}) + COS \xrightarrow{K_{4}} CO(X^{1}\Sigma^{+}) + S_{2}(x^{3}\Sigma_{a}^{-}), \tag{4}$$

$$2S(^{3}P_{i}) + M_{0} \stackrel{\kappa_{5}}{\rightarrow} S_{2}(X^{3}\Sigma_{g}^{-}, \sigma^{1}\Lambda_{g}, b^{1}\Sigma_{g}^{+}).$$

$$(5)$$

The following values are indicated for the rate constants of the reactions:

$$K_{x}/K_{z}=0.26,$$
 (2a)

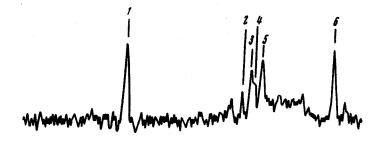
$$K_2 > 6.6 \cdot 10^{-11} \text{ cm}^{3} \cdot \text{sec}^{-1},$$
 (2b)

$$K_4 = 1.3 \cdot 10^{-14} \text{ cm}^{3} \cdot \text{sec}^{-1}$$
 (2c)

It is seen from the foregoing reactions that (2) and (5) can lead to the occurrence of S_2 in the metastable electronic state $^1\Sigma^+_g$, which could not be observed earlier by kinetic-spectroscopy methods [3].

This state lies 8.5×10^3 cm⁻¹ above the ground state $^3\Sigma_g^-$ [3], corresponding to a wavelength $^{\circ}1.18~\mu$. Transitions in which the vibrational number is

Microgram of the emission of a COS laser, obtained with an ISP-151 spectrograph with an electron-optical converter: 1) reference line λ = 1.014 μ (LG = 126 laser), 2 - 5) spectrum of COS laser (2 - 1.0920 μ , 3 - 1.0975 μ , 4 - 1.100 μ , 5 - 1.055 μ), 6) reference line λ = 1.1523 μ (PRK-4 mercury lamp).



decreased by unity occur in this case in the l.l- μ region, since the vibrational quantum in the lower state is equal to 725 cm⁻¹ [1]. Recognizing that the vibrational quantum in the upper state should be somewhat smaller, the appearance in the emission spectrum of several lines belonging to the series $v+l \rightarrow v$ becomes understandable.

It should be noted in conclusion that in spite of the fact that the photodissociation of COS (1) results mainly in sulfur atoms in the excited $^1\mathrm{D}_2$ states, no inversion via the most probable transition $^1\mathrm{D}_2$ \rightarrow $^3\mathrm{P}_2$ (λ = 1.08 μ) takes place. This is seen from the reaction rate constants given above. The S($^1\mathrm{D}_2$) state is annihilated at a rate higher than the annihilation rate of S($^3\mathrm{P}_2$), but the rates of population of these states differ insignificantly.

- [1] K.S. Sidhu, I.G. Csizmadia, O.P. Strausz, and H.E. Gunning, J. Am. Chem. Soc. 88, 2412 (1966).
- [2] H.E. Gunning, and O.P. Strausz, Adv. Photochem. 4, 143 (1966); O.P. Strausz, Chapter II: The Chemistry of Atomic Sulfur, Chem. Dep. Univ. Alberta, Edmonton, Canada, Preprint.
- [3] O.P. Strausz, R.J. Donovan, and M. de Sorgo, Ber. Bunsen Ges. <u>72</u>, 253 (1968).
- [4] G. Herzberg, Molecular Spectra and Atomic Structure, Vol. 1, Van Nostrand, 1950.

NATURE OF MAGNETOSTRICTION OF DYSPROSIUM AND OF ITS ALLOYS WITH GADOLINIUM

R.Z. Levitin, Yu.F. Popov, O.D. Chistyakov, and V.L. Yakovenko Moscow State University Submitted 6 July 1972 ZhETF Pis. Red. 16, No. 4, 224 - 228 (20 August 1972)

Recent investigations have shown that the magnetostriction of heavy rareearth metals (HREM) (with the exception of gadolinium) are quite high, on the order of 10^{-3} - 10^{-2} (cf., e.g., the review [1]). The nature of so large of a magnetostriction of the HREM, however, has not yet been explained. The most detailed studies were those of the magnetostriction deformations due to rotation of the magnetization vector in the basal plane of a hexagonal crystal [2 -4], and it was shown that the temperature dependence of these magnetostriction deformations are in satisfactory agreement with the value calculated theoretically for the model of one-ion anisotropy. Such an agreement, however, can not serve as proof of the one-ion nature of the magnetostriction. As shown in [5], the exchange interaction of the 4f electrons of HREM via the conduction electrons leads to the appearance of anisotropic interactions that depend on the state of only one ion, and therefore the magnetic anisotropy due to such an interaction should have a temperature dependence analogous to the dependence of the one-ion anisotropy. This conclusion can apparently be extended also to magnetostriction, since the anisotropic magnetoelastic interaction can be regarded as the deformation-dependent part of the magnetic-anisotropy energy.

To explain the nature of the magnetostriction of HREM, we measured the magnetostriction of dysprosium-gadolinium alloys. If the magnetoelastic interaction in HREM is of the one-ion type, then its value in the alloy can be regarded as the additive sum of the magnetoelastic interactions of the individual atoms, and the magnetostriction constants should depend in this case linearly on the concentrations of the alloy components. On the other hand, if the magnetoelastic interaction is of the exchange type, then it depends on the number of pairs of interacting atoms, and consequently the magnetostriction constants should