TABLE I

STABILITY CONSTANTS OF VARIOUS METAL–EDTA COMPLEXES

	⸻Log stability constant⸻	
Metal ion	Proposed method[a]	Literature[b]
Ba^{++}	7.9	7.76^c
Sr^{++}	8.7	8.63^c
Mg^{++}	8.9	8.69^c
Ca^{++}	10.7	10.59,^{e} 10.70,^{d} 10.96^d
Mn^{++}	13.8	13.58,^{d} 14.04,^{d} 13.79^d
Cd^{++}	16.4	16.59,^{d} 16.46^d
Zn^{++}	16.4	16.26,^{d} 16.50^d
Hg^{++}	22.1	21.80,^{d} 22.15^e

[a] 25.0°, in 0.1 N NaClO$_4$. [b] 20.0°, in 0.1 N KCl or KNO$_3$. [c] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947). [d] G. Schwarzenbach, R. Gut and G. Anderegg, *ibid.*, **37**, 937 (1954). [e] J. Goffart, G. Michel and D. Duyckaerts, *Anal. Chim. Acta*, **9**, 184 (1953).

(II)–ethylenediaminetetraacetate. In order to avoid this interference, the concentration of Hg–EDTA complex was lowered to 0.0001 M and the concentration of metal complex, MeY, increased to 0.01 M.

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ELECTRONIC AND VIBRATIONAL STATES OF THE NITRITE ION[1]

Sir:

The electronic spectrum of the nitrite ion has been studied under conditions of moderately high resolution, in an effort to determine the symmetry properties of the first excited singlet electronic state and the fundamental vibrational frequencies in the ground state and in the first excited state. The absorption spectrum of crystalline NaNO$_2$ at low temperature has been studied previously by other workers,[2,3] but a detailed analysis has not been offered. In agreement with Eberhardt and Trawick,[3] the origin of the lowest absorption transition at 25960 cm.$^{-1}$ is polarized perpendicular to the plane of the NO$_2^-$ ion, although the lattice and vibrational additions do show some absorption for light polarized in the plane of the NO$_2^-$ ion. The vibrational analysis of the absorption spectrum is quite straightforward. Long progressions of a single frequency of 632 ± 4 cm.$^{-1}$, with the intensity maximum in the fourth member of the progression, combine with single quantum additions of a frequency of 1018 cm.$^{-1}$ to each of the bands to account for all of the prominent bands in the transition. Irradiation of crystalline NaNO$_2$ at 77°K. with the λ 3650–3660 Å. lines of the mercury arc produced a weak but detectable fluorescence spectrum, which is reported here for the first time. The fluorescence and absorption spectra have a common origin, and are mirror images of each other. Long progressions of a frequency of 829 cm.$^{-1}$, with the intensity maximum also in the fourth member of the progression combine with single quantum additions of a 1337 cm.$^{-1}$ frequency to each of the bands in the progression.

Since the absorption and fluorescence spectra possess a common origin, the electronic transition must be allowed by symmetry. The symmetry of the site, crystal and molecule are all C$_{2v}$,[4] so the O–O band cannot be induced by the crystal. The polarization properties then prove that the transition is allowed by symmetry and is polarized perpendicular to the NO$_2^-$ plane, in complete agreement with the predictions of Walsh for an 18-electron molecule of C$_{2v}$ symmetry,[5] but in disagreement with recent predictions by McGlynn and Kasha.[6] In further agreement with Walsh, calculations based on the method of Craig[7] indicate that the bond angle has increased slightly in the excited state.

Vibrational assignments for the NO$_2^-$ ion in crystalline NaNO$_2$ are given in Table I for the ground electronic state and for the first excited singlet electronic state. The vibrational frequencies deduced from the analysis of the fluorescence spectrum agree within the limits of error with the frequencies observed in infrared absorption. It should be noted that ν_3 is lower in frequency than ν_1, in agreement with the Raman polarization studies of Langseth and Walles.[8] The resemblance with ozone[9] in this respect is apparent.

TABLE I

VIBRATIONAL FREQUENCIES OF NO$_2^-$

	Ground electronic state (0 cm.$^{-1}$)	Excited electronic state (25960 cm.$^{-1}$)
ν_1, symmetric stretching	1337 ± 4	1018 ± 4
ν_2, bending	829 ± 2	632 ± 4
ν_3, asymmetric stretching	1270 ± 4	Not obsd.

It is hoped that additional work at 4°K. which is now in progress will lead to a detailed analysis of the lattice and vibrational states of the NO$_2^-$ ion, and that a complete analysis may eventually be obtained from studies of N^{15}O$_2^-$.

(4) G. B. Carpenter. *Acta Cryst.*, **5**, 132 (1952).

(5) A. D. Walsh. *J. Chem. Soc.*, 2280 (1953).

(6) S. P. McGlynn and M. Kasha. *J. Chem. Phys.*, **24**, 481 (1956).

(7) D. P. Craig. *J. Chem. Soc.*, 2146 (1950).

(8) A. Langseth and E. Walles. *Z. physik. Chem.*, **B27**, 209 (1934).

(9) R. M. Badger and M. K. Wilson, *J. Chem. Phys.*, **18**, 998 (1950).

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(1) Supported by the Office of Ordnance Research. under Contract DA-30-115-Ord-620 with the University of Rochester.

(2) G. Rodloff, *Z. Physik*. **91**, 511 (1934).

(3) W. H. Eberhardt and W. G. Trawick. *J. Chem. Phys.*, **22**, 1462 (1954).

VAPORIZATION OF BORIC OXIDE AND THERMODYNAMIC DATA FOR THE GASEOUS MOLECULES B$_2$O$_3$, B$_2$O$_2$ AND BO

Sir:

Vaporization of liquid B$_2$O$_3$ at high temperatures has been difficult to interpret since there has been uncertainty about the molecular species involved in the process. Recent mass spectrographic studies,[1,2] together with effusion[3] and flow[4] vapor

(1) P. Bradt, NBS Report 3016. Jan. 1. 1954.

(2) W. A. Chupka, R. F. Porter and M. G. Inghram, *J. Chem. Phys.*, in press (1956).

(3) R. Speiser, S. Naiditch and H. L. Johnston, THIS JOURNAL, **72**, 2578 (1950).

(4) (a) J. R. Soulen, P. Sthapitanonda and J. L. Margrave. *J. Phys. Chem.*, **59**, 132 (1955); (b) J. R. Soulen, Ph.D. Thesis, University of Wisconsin, 1955.

pressure studies, and direct boiling point[4b] measurements now make it certain that at temperatures up to 2400°K. the vaporization process primarily involves the formation of $B_2O_3(g)$ with less than 5.0% of $B_2O_2(g)$, $BO(g)$, or gaseous elements. The absorption and emission spectra of the equilibrium gas we have found to be identical with those obtained from boric acid–methyl alcohol flames and to correspond to the "Boric Acid Fluctuation Bands" discussed by Pearse and Gaydon.[5] Thus, the green color of boron flames must be associated with an electronic transition in the $B_2O_3(g)$ molecule.

On the basis of a highly symmetrical model for $B_2O_3(g)$ in which the two borons are on opposite sides of an equilateral triangle of oxygen atoms and with estimated bond angles and distances, one may calculate free energy functions and heat content functions. These, coupled with vapor pressure data, allow evaluation of the heat of sublimation of boric oxide and the heat of formation of $B_2O_3(g)$. In addition, our data and those of Chupka, Porter, and Inghram[2] yield values of useful thermodynamic properties for gaseous boron oxides as given in Table I. These values indicate that $BO(g)$ is considerably less stable than suggested by Searcy and Meyers[6]; they overestimated the stability of $BO(g)$ because they did not consider $B_2O_2(g)$ as important in the high temperature reduction of MgO with B. Earlier work of Searcy[7] on the reduction of BeO with B is more reliable since $B_2O_2(g)$ is less important at the higher temperatures.

TABLE I

THERMODYNAMIC PROPERTIES OF GASEOUS BORON OXIDES[a]

Molecule	ΔH_f at 0°K., kcal./mole	Dissociation energy to gaseous atoms at 0°K., kcal./mole
BO(g)	$\geqslant +5.3$	≤ 189.5 (8.2 ev.)[b]
$B_2O_2(g)$	-110.9 ± 7	500.5 ± 10
$B_2O_3(g)$	-214.4 ± 5	662.9 ± 6

[a] The heat of sublimation of boron at 0°K. was taken as 135.8 kcal./mole (Alan W. Searcy, private communication 1955); the heat of formation of $B_2O_3(s)$ at 0°K. as -303.8 (data from NBS Report 3456, 1954 corrected to 0°K.); and the dissociation energy of oxygen as 117.96 kcal./mole (L. Brewer, private communication, 1955). [b] Previous values for D(BO) are 9.1 e.v from a linear Birge–Sponer extrapolation with the 0–11 vibrational levels of the ground state suggested by G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950, and 7.6 ± 0.4 ev. suggested by A. G. Gaydon, "Dissociation Energies," Chapman and Hall, Ltd., London, 1953.

Our identification of the green emission and absorption bands with the $B_2O_3(g)$ molecule is confirmed by a photometric study of the variation of the intensity of the absorption of the equilibrium gases over liquid boric oxide as a function of temperature. From the slopes of log IT vs. $1/T$ plots we reproduce the heat of sublimation of the gaseous molecule responsible for the green bands as 78 ± 15 kcal./mole while the effusion vapor pressure data lead to a value of 77.6 kcal./mole for

(5) R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 60–61.

(6) A. W. Searcy and C. E. Meyers, Technical Report on Contract No. N7onr-394/12, Project No. NR-032-331, June, 1953.

(7) A. W. Searcy, University of California Radiation Lab. Report UCRL-1404 (1951).

$B_2O_3(g)$ over the same temperature range. The fact that we can observe the bands in absorption at 1543°K. eliminates the possibility suggested by Singh[8] that these are $BO(g)$ bands involving the $B^2\Sigma^+$ and a higher electronic state. The Boltzmann factor would allow no appreciable population in the absorbing state. In addition, other well-known $BO(g)$ spectra should be observable in absorption if boric oxide underwent extensive decomposition on vaporization.

(8) N. L. Singh, (a) Proc. Ind. Acad. Sci., 29A, 424 (1949); (b) J. Sci. Res. Banaras Hindu Univ., 2, 147 (1951–1952).

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CORTICAL STEROIDS SUBSTITUTED AT C_{12}

Sir:

The introduction of halogen and other functionality at position 9 has been shown to produce important effects on the physiological properties of the parent cortical steroids as manifested in the case of the 9α-fluoro analogs by a large enhancement of both glucocorticoid and mineralocorticoid activity.[1] To date the effect of fluorine substitution at positions other than C_9 has not been reported.[2] In this communication we wish to describe a number of corticosterone and 11-dehydrocorticosterone systems substituted at position 12.
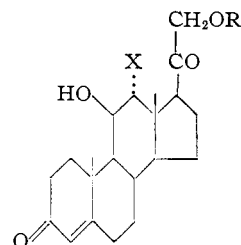
IVa, X = Br; IVb, X = Cl
IVc, X = F; IVd, X = F, Δ^1
IVe, X = F, 11 C = O;
IVf, X = OH

12α-Bromo-11-dehydrocorticosterone acetate (I)[3] was converted to its 3,20-disemicarbazone derivative, m.p. >300°; $\lambda_{max.}^{CH_3OH}$ 269 mμ (30,300), shoulder 245–250 mμ (25,200); (N, 14.8; Br, 13.7), and the latter reduced at C_{11} with lithium borohydride in tetrahydrofuran[4] followed by removal of the semicarbazone residues to give 12α-bromocorticosterone, IVa (R = H), m.p. 215–219° (dec.); $[\alpha]^{CHCl_3}D$ +126°, $\lambda_{max.}^{CH_3OH}$ 240 mμ (16,300); $\lambda_{max.}^{CHCl_3}$ 2.90, 5.87, 6.02, 6.18, μ (C, 59.75; H,

(1) (a) J. Fried and E. Sabo, THIS JOURNAL, 75, 2273 (1953); (b) J. Fried, K. Florey, E. Sabo, J. Herz, A. Restivo, A. Borman and F. M. Singer, ibid., 77, 4181 (1955), and earlier references cited therein; (c) R. F. Hirschmann, R. Miller, R. E. Beyler, L. H. Sarett and M. Tishler, ibid., 77, 3166 (1955); (d) A. Nobile, W. Charney, P. L. Perlman, H. L. Herzog, C. C. Payne, M. E. Tully, M. A. Jevnik and E. B. Hershberg, ibid., 77, 4184 (1955); (e) J. A. Hogg, F. H. Lincoln, A. H. Nathan, A. R. Hanze, W. P. Schneider, P. F. Beal and J. Korman, ibid., 77, 4438 (1955); (f) E. Vischer, C. Meystre and A. Wettstein, Helv. Chim. Acta, 38, 1502 (1955).

(2) J. E. Herz, J. Fried and E. F. Sabo have recently reported the preparation and physiological properties of 12α-halo-11β-hydroxyprogesterone, THIS JOURNAL, 78, 2017 (1956).

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