

TABLE I
STABILITY CONSTANTS OF VARIOUS METAL-EDTA COM-
PLEXES

Metal ion	Log stability constant	
	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, ^c 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 NaClO₄. ^b 20.0°, in 0.1 N KCl or KNO₃. ^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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA
RECEIVED FEBRUARY 20, 1956

R. W. SCHMID
CHARLES N. REILLEY

ELECTRONIC AND VIBRATIONAL STATES OF THE NITRITE ION¹

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 NaNO₂ 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 NO₂⁻ ion, although the lattice and vibrational additions do show some absorption for light polarized in the plane of the NO₂⁻ 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 NaNO₂ 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

(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).

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 NO₂⁻ 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 Craig⁷ indicate that the bond angle has increased slightly in the excited state.

Vibrational assignments for the NO₂⁻ ion in crystalline NaNO₂ 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 ν₃ is lower in frequency than ν₁, in agreement with the Raman polarization studies of Langseth and Walles.⁸ The resemblance with ozone⁹ in this respect is apparent.

TABLE I
VIBRATIONAL FREQUENCIES OF NO₂⁻

	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 NO₂⁻ ion, and that a complete analysis may eventually be obtained from studies of N¹³O₂⁻.

(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).

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF ROCHESTER
ROCHESTER 20, NEW YORK

JEROME W. SIDMAN

RECEIVED APRIL 10, 1956

VAPORIZATION OF BORIC OXIDE AND THERMO- DYNAMIC DATA FOR THE GASEOUS MOLECULES B₂O₃, B₂O₂ AND BO

Sir:

Vaporization of liquid B₂O₃ 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 effusion³ and flow⁴ 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.