Erratum: Statistical Mechanics of Isotope Effects on the Thermodynamic Properties of Condensed Systems

Jacob Bigeleisen

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produced the maxima and minima under the conditions of the original investigation, but obviously the detailed explanation of this spectral structure put forth by us in the original paper[2] no longer applies.

The absorption spectrum of the fully deuterium-substituted molecule has now been observed under closely similar conditions to those used in the measurement of the disiloxane spectrum. A broad featureless band occurs with maximum absorption at a position indistinguishable under the conditions of the observations from that of the disiloxane band, and with nearly the same absorptivity. The two bands have closely similar shapes, though the absorption of disiloxane-d_6 appears to be somewhat stronger on the low-frequency side. The two band contours are compared in Fig. 1, and show that there is little difference between them, as would be expected if the absorption is due almost entirely to the motion of the oxygen atom.

Although the above results are rather indefinite in their structural implications, the low frequency of the absorption maximum, taken together with the very wide Si—O—Si bond angle (near 150°), does indicate a flat and anharmonic potential function for the bending motion. Thus the motion must be treated with due consideration of the special shape of the potential function characteristic of the quasi-linear molecule, as has been done by Thorson and Nakagawa.[4] However resolution of the fine structure predicted by them, which our earlier work[2] seemed to have verified, will apparently require considerably higher resolving power than is presently available to us, and possibly also a study of the molecule at greatly reduced temperatures.

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[1] R. C. Lord and T. K. McCubbin, Jr., J. Opt. Soc. Am. **47**, 689 (1957).
[2] J. R. Aronson, R. C. Lord, and D. W. Robinson, J. Chem. Phys. **33**, 1004 (1960).
[3] D. W. Robinson, J. Opt. Soc. Am. **49**, 966 (1959).
[4] W. R. Thorson and I. Nakagawa, J. Chem. Phys. **33**, 996 (1960).

Erratum: Magnetic Properties and Optical Absorption Spectrum of K_2ReCl_6

J. C. EISENSTEIN

National Bureau of Standards, Washington, D. C.

DR. W. A. Runciman has kindly pointed out to me that in Table III the matrix element between the second $^2E_\gamma\epsilon^2$ state and the first $^4T_1\gamma\epsilon^2$ state should be $\frac{1}{6}\sqrt{3}\zeta$ instead of $\frac{1}{3}\sqrt{3}\zeta$. This mistake does not appear in the manuscript or the galley proofs; the numerical results of the paper are therefore unaffected.

Erratum: Statistical Mechanics of Isotope Effects on the Thermodynamic Properties of Condensed Systems

JACOB BIGELEISEN

Chemistry Department, Brookhaven National Laboratory Upton, Long Island, New York

DR. Marvin Stern has kindly called my attention to the following errata in the manuscript:

(1) Multiply right-hand side of Eq. (3.9) by N^{-1};

(2) Eq. (3.14), replace $(\lambda_{ic}{}^{0\prime})^{2j}$ by $(\lambda_{ic}{}^{0\prime})^{j}$;

(3) Eq. (3.15), replace $(4\pi^2 N)^{-1}\Sigma\nu_{ic}{}^{0\prime}(\lambda_{ic}{}^{0\prime})^{j}$ by $N^{-1}\Sigma\nu_{ic}{}^{0\prime}(\lambda_{ic}{}^{0\prime}/4\pi^2)^{j}$;

(4) Eq. (3.18), write $u_{ib}{}' > 2\pi$;

(5) Eqs. (4.21) and (4.22). Each term on the right-hand side should contain the factor $\beta\gamma$.

(6) In the equation in the middle of page 1492, $\gamma = \alpha V/\beta C_v$, α is used in the conventional manner as the symbol for the coefficient of expansion, and not as the compressibility. The conventional symbol β has already been used for the compressibility;

(7) Eq. (6.2), replace F by G.

Erratum: Comprehensive Investigation of the Electronic Spectroscopy and Theoretical Treatments of Ferrocene and Nickelocene

DONALD R. SCOTT AND RALPH S. BECKER

Department of Chemistry, University of Houston, Houston 4, Texas

THE majority of the following corrections were necessitated by the discovery of an error in group theoretical notation for the $4p_z$ orbital in the D_{5d} point group. This error also occurs in the original references 1, 12, 16, and 17 as well as in other publications.[1] The correct notation for the $4p_z$ orbital in the D_{5d} group is a_{2u} instead of a_{1u}.

In Fig. 5, the $4p(a_{1u})$ levels of Moffitt and of Dunitz and Orgel should read $4p(a_{2u})$. In Figs. 6 and 7, the $\tilde{p}(a_{1u})$ level of Liehr and Ballhausen should read $\tilde{p}(a_{2u})$.

In Table VII, line 2 should read a_{2u} for a_{1u} under D_{5d}. In Table IX under Moffitt, line 9 should read $4p(a_{2u})$ for $4p(a_{1u})$. In Table IX under Dunitz and Orgel, line 9 should read $4p(a_{2u})$ for $4p(a_{1u})$. In Table X under Dunitz and Orgel, line 2 should read $e_{1g}-4p(a_{2u})$ for $e_{1g}-4p(a_{1u})$. Line 9, $[e_{1u}-4p(a_{1u})]$, should

be entirely omitted. Add to this section of Table X

$$a_{1g} - 4p(a_{2u}) \qquad 22\ 600 \qquad z$$

In Table X under Moffitt, add

$$h(a_{1g}) - 4p(a_{2u}) \qquad 31\ 000 \qquad z$$

In Table XI under Moffitt, line 6 should read $3d(e_{2g}) - 4p(a_{2u})$ instead of $3d(e_{2g}) - 4p(a_{1u})$. In Table XI under Dunitz and Orgel, line 4 should read $e_{1g} - 4p(a_{2u},\ e_{1u})$ instead of $e_{1g} - 4p(a_{1u},\ e_{1u})$. Line 8 should be omitted and replaced by

$$4400 \quad e_{2g} - e_{1g}' \quad (Cp+3d) - (Cp+3d) \quad 19\ 800 \quad \text{No.}$$

On page 526, paragraph 3, the next to last line should read $4p(a_{2u})$ for $4p(a_{1u})$. In the first sentence of paragraph 4, the word three should be replaced by four. On page 527, paragraph 3, line 8 should read $4p(a_{2u})$ instead of $4p(a_{1u})$. The last line of this paragraph should read: The 4400 A (22 730 cm^{-1}) band is assigned as the forbidden $e_{2g} - e_{1g}'$ transition. On page 530, the first line of paragraph 3 should read 4400 A for 4000 A. On the same page, paragraph 7, line 7 should read $4p(a_{2u})$ for $4p(a_{1u})$.

[1] L. E. Orgel, *An Introduction to Transition Metal Chemistry Ligand Field Theory* (Methuen & Company, Ltd., London, 1960), Table 10.3.2, p. 157; D. Brown, J. Chem. Phys. **29**, 1086 (1958).

Notes

Identification of an Electronic Transition of $N_2{}^{2+}$

P. K. CARROLL

Laboratory of Molecular Structure and Spectra, Department of Physics, The University of Chicago, Chicago, Illinois

AND

A. C. HURLEY

Division of Chemical Physics, C.S.I.R.O., Chemical Research Laboratories, Melbourne, Australia

(Received August 7, 1961)

A NEW headless band with origin at 1589.745 A was recently observed in a hollow cathode discharge through pure nitrogen at low pressure.[1] From the rotational structure of the band it was deduced that

(a) The emitter is certainly molecular nitrogen (because of the observed intensity alternation).

(b) The band arises from a $^1\Sigma \rightarrow ^1\Sigma$ or $^2\Sigma \rightarrow ^2\Sigma$ transition, the lower state being either $\Sigma_g{}^+$ or $\Sigma_u{}^-$.

(c) It is probably a 0—0 band. No other hands of the transition were observed.

Since the B values showed that the $v=0$ level of none of the states of N_2 or $N_2{}^+$ with known B_0 values was involved, several hitherto unobserved states of N_2, $N_2{}^+$, and $N_2{}^{2+}$ were considered but a definite assignment could not be made on the basis of the spectrum alone.

TABLE I. Calculated and observed parameters.

	Transition $d\ ^1\Sigma_u{}^+ \rightarrow a\ ^1\Sigma_g{}^+$ of $N_2{}^{2+}$			
	Calculated by Method (a)	Method (b)		Analysis of 1590A band
ν_0	67629	64080	ν_0	62903.18
r_e'	1.027	1.165	r_0'	1.1363
r_e''	1.032	1.153	r_0''	1.1316
ω_e'	1867	1404	ω_0' [a]	(1910)
ω_e''	2108	1635	ω_0'' [a]	(1960)
D_e' [a]	12.9×10^{-6}	11.3×10^{-6}	D_0'	7.1×10^{-6}
D_e'' [a]	10.4×10^{-6}	8.9×10^{-6}	D_0''	6.9×10^{-6}

[a] From $D = 4B^3/\omega^2$.

One of the possibilities considered was that the band might be the 0—0 transition of the $^1\Sigma_u{}^+ \rightarrow ^1\Sigma_g{}^+$ system of $N_2{}^{2+}$ which would be analogous to the Mulliken system of C_2. As a theory has recently been developed[2] which enables the potential curves for doubly positive diatomic ions to be calculated, this possibility has now been examined more closely. The theory relates the binding energy $B_d(R)$ of a doubly charged ion (in this case $N_2{}^{2+}$) to the binding energy $B_n(R)$, of the corresponding state of the isoelectronic molecule (C_2) by means of the equation

$$B_d(R) = -(1/R) + t^2 B_n(tR), \qquad (1)$$

where t is a scaling parameter (see below).

The $B_n(R)$ curves for the $a\ ^1\Sigma_g{}^+$ and $d\ ^1\Sigma_u{}^+$ states of C_2 were derived as Morse functions going to the limits $C(^3P) + C(^3P)$ and $C(^1D) + C(^1S)$, respectively, assuming $D_0[C_2(a\ ^1\Sigma_g{}^+)] = 6.50$ ev^3 and taking the other parameters from Herzberg.[4] The potential curves for the corresponding states of $N_2{}^{2+}$ were then calculated from Eq. (1) using the two different values of the parameter t proposed in reference 2.

(a) In the first calculation $t = [T_{d,v}(\infty)/T_{n,v}(\infty)]^{\frac{1}{2}}$, where $T_{d,v}(\infty)$ is the kinetic energy of the valence shell electrons for the appropriate states of the separated ions $N^+ + N^+$ and $T_{n,v}(\infty)$ is the same quantity for the separated atoms $C + C$.

(b) In the second calculation, $t = [T_d(\infty)/T_n(\infty)]^{\frac{1}{2}} = [E_d(\infty)/E_n(\infty)]^{\frac{1}{2}}$, where $T_d(\infty)$ and $T_n(\infty)$ are the total kinetic energies of the appropriate states of $N^+ + N^+$, $C + C$, respectively, and $E_d(\infty)$ and $E_n(\infty)$ are the experimental total energies of these states.

The resulting $N_2{}^{2+}$ potential curves are all qualitatively of the form shown in reference 2 (Figs. 1 and 2). For small nuclear separations there is a local energy minimum lying well above the dissociation limit. With increasing nuclear separation each curve rises to a maximum more than 1 ev above the minimum and then falls smoothly to the dissociation limit. Because of the height and breadth of the maxima, tunneling may be neglected at least for the lower vibrational levels and the quantities r_e', r_e'', ω_e', ω_e'', ν_e and ν_0 for