Photoelectron spectrum and structure of B₂O₂

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The He I photoelectron spectrum of B_2O_2 is presented. A comparison of *ab initio* molecular orbital calculations and the observed spectrum provides the most conclusive evidence to date that the geometrical structure is $D_{\infty h}$ O=B–B=O. Even though the experiment is conducted at 1200 °C, vibrational structure is evident in the first two bands. A complex Franck–Condon fitting is used to infer the geometrical changes occurring when the various ionic states are formed. The results are in fairly good agreement with Δ SCF calculations. The orbital ordering in B_2O_2, $\pi_g, \pi_u, \sigma_g, \sigma_u$ differs from that in the isoelectronic molecule C_2N_2.

INTRODUCTION

It has been known for some time[1] that the gaseous species B_2O_2 is generated when a mixture of boron and B_2O_3 is heated to ~ 1200 °C. At that time, the molecular structure of B_2O_2 was assumed to be linear symmetric O=B–B=O, isoelectronic with cyanogen. Subsequently, an alternative structure,

O – B=O
B
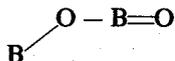
was proposed,[2] based on bond energy considerations. The topologies of these structures were examined by *ab initio* calculations[3] at the STO-3G level and by a semiempirical (MNDO) method.[3] Both calculations[3] showed O=B–B=O to be more stable, but "new, preferably more direct evidence" was sought.[4]

The strongest support for the O=B–B=O structure comes from infrared spectroscopy of the matrix-isolated species. Only two frequencies of the fundamental vibrations have been observed,[5,6] which is consistent with a $D_{\infty h}$ structure. Alternative structures such as

$$D_{2h} \left[O \underset{B}{\overset{B}{\diamond}} O \right] \quad C_{\infty v} [\text{B–O–B–O}]$$

or

$$C_s \left[B \diagup \overset{\text{O–B=O}}{} \right]$$
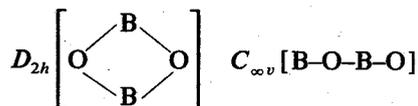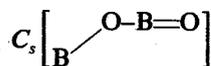
would be expected to have three, five, or six infrared active frequencies, respectively. However, this criterion alone would not rule out the $D_{\infty h}$ structure BOOB.

The infrared experiments were apparently done thoroughly, including several isotopic substitutions. From the isotopic shifts and a normal coordinate analysis, the unobserved frequencies were calculated[6] assuming the $D_{\infty h}$ structure. However, one can never be absolutely certain if the unobserved frequencies are forbidden or just very weak, and hence molecular structure determinations based on unobserved frequencies must retain some doubt.

An electron diffraction study would be helpful in establishing not just the symmetry, but the internuclear distances as well. To our knowledge, such a study has not been reported.[7] The approach we shall describe below combines photoelectron spectroscopy with high quality *ab initio* calculations. The calculations are performed for several possible geometries of B_2O_2 and the preferred one is determined by the total energy criterion. In addition, the ionization energies are computed and compared with those obtained in the photoelectron spectrum. One match is found to be much better than the others, and corroborates the conclusion from the total energy criterion. With the structure established, the combination of PES and calculations is used to determine the symmetry and sequence of the valence molecular orbitals, their character (bonding or antibonding) and the change in geometry that ensues upon ionization. The geometry change is determined both by the *ab initio* calculation of the cation states and by a polyatomic Franck–Condon fitting of the experimental spectrum which includes Boltzmann terms.

II. EXPERIMENTAL ARRANGEMENT

The hemispherical electron energy analyzer and oven system for generating high temperature vapors which we have used in this experiment were described previouly.[8] A tungsten oven was used, and temperature was measured with a chromel-alumel thermocouple. The vaporization temperature was approximately 1500 K.

The sample consisted of an equimolar mixture of powdered boron and B_2O_3, thoroughly mixed. Both substances were of commerical origin. The mixture was baked out *in situ* and the spectrum monitored as the temperature was increased. Ar and Xe gases were periodically introduced as calibrants for the energy scale. Evolution of H_2O was observed, even at the temperatures when B_2O_2 spectra were obtained. Individual spectra were collected with the aid of an LSI 11/23 computer, recorded on mass storage media, and subsequently summed to improve the signal to noise ratio. The energy scale is accurate to ± 0.02 eV.

III. EXPERIMENTAL RESULTS

The He I photoelectron spectrum obtained is shown as experimental points in Fig. 1. It consists of four bands attri-

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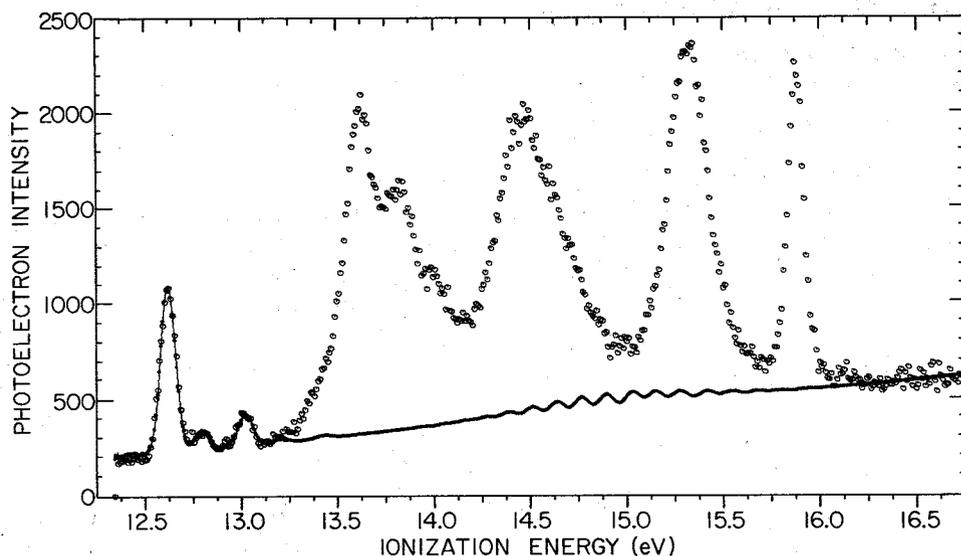
FIG. 1. He I photoelectron spectrum of B_2O_2 obtained at 1200 °C. ◯—Experimental data. Smooth line—H_2O impurity and linearly increasing background, which is subsequently subtracted.

buted to B_2O_2, with peak maxima at 13.61, 14.45, 15.33, and 15.88 eV, together with the first band of H_2O, with its (0,0,0) →(0,0,0) transition at 12.62 eV. The width of this latter transition is ~ 85 meV (FWHM), essentially the same as that of the 15.85 eV band. This establishes an upper limit to the resolution of the apparatus at ~ 1500 K. Vibrational structure can be noted not only on the H_2O band, but also on the first band of B_2O_2 and probably on the second band.

The appearance potential of $B_2O_2^+$ from B_2O_2 by electron impact has been reported[9] to be 13.37 ± 0.34 eV. The onset of the first band in Fig. 1 attributable to B_2O_2 is ~ 13.3 eV, and presumably contains some hot band contributions (*vide infra*). The good agreement confirms our assignment of the 13.61 eV band to B_2O_2; since all four bands maintained their relative intensity throughout all the runs, they can safely be attributed to the same species.

The observation of vibrational structure in the photoelectron spectrum of a vapor at 1500 K, without use of a diluent gas to relax the vibrational excitation, is unusual. It can be understood as the fortuitous combination of moderately good resolution (considering the temperature) and relatively large vibrational quanta in the sample species, both as neutral and ion. The latter condition is a consequence of rather strong bonds and low reduced masses.
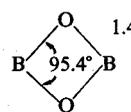
IV. INTERPRETATION OF RESULTS

A. Relative stability of various B_2O_2 structures

Ab initio molecular orbital calculations using the GAUSSIAN 80[10] and GAUSSIAN 82[11] programs were carried out to determine the relative stabilities of various possible B_2O_2 structures. Geometries were optimized subject to certain symmetry constraints. Initial calculations performed at the STO-3G level[12] are summarized in Table I. The conclusions from this exploratory calculation are that the O=B–B=O structure is most stable, the B–O–B–O structure 1.79 eV less stable, and the other two structures much less stable. The relative stabilities and internuclear distances for O=B–B=O and B–O–B–O were identical to those previously reported[3] at the STO-3G level. However, when the

energy minima for these two structures were determined with the larger 4-31G basis set[13] the B–O–B–O structure was only 0.73 eV less stable; with the still larger 6-31G* basis set,[14] it was 0.87 eV less stable. These more extensive calculations, summarized in Table II, appear to make the relative stability of O=B–B=O and B–O–B–O less certain from a purely calculational perspective since correlation effects could conceivably reverse the final results. Therefore, the calculations were pursued at the 6-31G* level to third order in Møller–Plesset perturbation theory,[15] using the 6-31G* optimized structures. The relative stability of O=B–B=O increased to 1.28 eV. Missing correlation effects would not be expected to change this value significantly, making the conclusion about relative stability from a purely calculational view fairly certain. The fundamental vibrational frequencies of the neutral ground state were computed for both O=B–B=O and B–O–B–O structures, and are compared with the experimentally derived values of Serebrennikov[6] in Table III. The calculated O=B–B=O frequencies are closer to the experimental values, which can be considered confirmatory evidence, though not conclusive by itself. (Of course,

TABLE I. Relative stability of B_2O_2 structures based on *ab initio* STO-3G calculations.

Structure (r in Å)			Relative energy (eV)	Symmetry constraints	Final symmetry
O = 1.176	B–B 1.610	= O 1.176	0[a]	C_s	$D_{\infty h}$
B – 1.280	O–B 1.319	– O 1.186	+ 1.79	C_s	$C_{\infty v}$
B – 1.278	O–O 1.341	– B 1.278	+ 9.24	C_s	$D_{\infty h}$
O B ⟨95.4°⟩ B 1.416 O			+ 12.12	D_{2h}	D_{2h}

[a] Energy = − 196.530 10 a.u.

TABLE II. *Ab initio* geometries[a] and energies of O=B–B=O and B–O–B–O at various levels of calculation.

		$r_1(\text{Å})$	$r_2(\text{Å})$	$r_3(\text{Å})$	E (a.u.)	Relative stability (eV)
HF/4-31G	OBBO	1.196	1.631	1.196	−198.895 94	0
	BOBO	1.337	1.314	1.202	−198.869 20	0.73
HF/6-31G*	OBBO	1.182	1.668	1.182	−199.184 92	0
	BOBO	1.306	1.311	1.189	−199.153 18	0.86
MP3/6-31G*	OBBO[b]	(1.182)	(1.668)	(1.182)	−199.682 21	0
	BOBO[b]	(1.306)	(1.311)	(1.189)	−199.635 22	1.28[c]
	OBBO	1.201	1.647	1.201	−199.683 75	⋯

[a] r_1, r_2, r_3 correspond to bond lengths from left to right.
[b] HF/6-31G* geometry.
[c] Optimization of both structures should not change the relative energy by more than about 0.05 eV.

all five frequencies of B–O–B–O should be infrared active, as noted earlier, and only two have been observed).

B. Comparison of calculated and experimental energies

The ionization energies for several valence bands of the two structures (O=B–B=O and B–O–B–O) were calculated at three levels of sophistication: (a) Koopmans' theorem; (b) Δ SCF vertical (calculating the energy of the ionic state at the neutral molecule geometry); and (c) Δ SCF adiabatic (calculating the energy of the ionic state at its relaxed geometry). The calculations on the ions were done using a spin restricted open shell procedure[16] and symmetry restricted wave functions.

The results of these calculations are summarized in Table IV. The agreement between the calculated O=B–B=O vertical ionization energies and the experimental values is quite good at the 4-31G level, much better than with the corresponding B–O–B–O calculated energies. This is particularly true of the absolute values of the first two ionization energies and their spacing. (Experiment: 13.61, 14.45; O=B–B=O structure: 13.72, 14.64; B–O–B–O structure: 9.60, 11.59). In addition, the area of the first band in the experimental spectrum is the largest of the four bands, which makes it the most likely candidate to assign to ionization from a π orbital. This assignment is consistent with the O=B–B=O structure, but not with the B–O–B–O structure. Of the various arguments marshalled in this article in support of the O=B–B=O structure, we view the above two as most convincing.

TABLE III. Calculated and experimental frequencies of B₂O₂ (cm⁻¹).

	$\omega_1(\Sigma)$	$\omega_2(\Sigma)$	$\omega_3(\Sigma)$	$\omega_4(\Pi)$	$\omega_5(\Pi)$
Experimental[a]	2060	585	1897.8	410	213
O=B–B=O, MP3/6-31G*	2222	628	2052	432	216
O=B–B=O HF/4-31G	2253	639	2031	547	236
B–O–B–O, HF/4-31G	2206	843	1458	553	176

[a] Reference 6.

Several attempts were made to observe the fifth band, predicted to occur at ∼ 19 eV. In some spectra a rather broad band was observed above the rising background, much weaker than the other bands. Since we are not certain that this band is attributable to B₂O₂, we have not considered it further.

C. Franck–Condon fitting of experimental spectrum

If one has a photoelectron spectrum of a diatomic molecule which has completely resolved vibrational structure, and the transition initiates in $v''=0$ of the neutral state, then it is a straightforward matter to apply the Franck–Condon principle to determine the change in internuclear distance characterizing this transition. If the neutral molecule has significant vibrational excitation, the Franck–Condon calculation must be convoluted with a Boltzmann distribution. If the vibrational structure is not completely resolved, the instrumental resolution must be incorporated, and some form of fitting to the experimental spectrum must be adopted. Finally, if one has a polyatomic molecule to contend with, the Franck–Condon problem can rapidly increase in complexity, especially if the bands overlap each other. In general, only totally symmetric vibrations will be Franck–Condon active, although there are some exceptions. For O=B–B=O, there are two totally symmetric (Σ_g^+) vibrations.[17]

The Franck–Condon fitting procedure is outlined in more detail in the Appendix. We describe below its application to the B₂O₂ spectrum of Fig. 1. First, the impurity H₂O spectrum was subtracted. (Note that the obscured second band of H₂O was simulated as shown, and also subtracted.) The H₂O spectrum was synthesized using our experimental resolution, known frequencies,[18] estimated coupling parameters (by measuring relative intensities in published spectra[19,20]) and a Boltzmann distribution for 1500 K. Next, a linearly rising background, shown together with the water impurity in Fig. 1, was subtracted. The residual B₂O₂ spectrum, shown as experimental points in Fig. 2, was submitted to a least-squares fitting of the four observed bands. The temperature was set to 1500 K, the instrumental resolution was taken to be 85 meV FWHM, and the totally symmetric vibrational frequencies of the neutral molecule (2060 and

TABLE IV. Calculated and experimental ionization energies of B_2O_2.

State	I.P. from Koopmans' theorem (eV)			Vertical I.P. from Δ SCF (eV)		Vertical I.P.[a] Expt. (eV)	Adiabatic I.P. from Δ SCF (eV)		Adiabatic I.P.[b] Expt. (eV)
	STO-3G	4-31G	6-31G*	STO-3G	4-31G		STO-3G	4-31G	
A. O=B–B=O structure									
$(\pi_g)^{-1}$	11.81	14.68	14.63	11.31	13.72	13.61	10.94	13.58	13.58
$(\pi_u)^{-1}$	12.81	15.38	15.21	12.55	14.64	14.45	12.20	14.48	14.21
$(\sigma_g)^{-1}$	13.84	17.29	17.23	13.32	16.16	15.33	13.20	16.10	15.28
$(\sigma_u)^{-1}$	14.72	17.86	17.90	13.82	16.51	15.88	13.77	16.49	15.88
$(\sigma_g)^{-1}$	16.81	19.62	19.39						
$(\sigma_g)^{-1}$	35.16	37.60	37.08						
B. B–O–B–O structure									
$(\sigma)^{-1}$	7.44	10.77	10.73		9.60				
$(\pi)^{-1}$	11.23	14.00	14.12		11.59				
$(\sigma)^{-1}$	14.20	17.00	17.23		13.58				
$(\pi)^{-1}$	15.53	18.42	18.61						
$(\sigma)^{-1}$	21.52	25.02	25.35						
$(\sigma)^{-1}$	34.86	36.90	36.50						

[a] Corresponds to maximum of band.
[b] Obtained from Franck–Condon fitting.

585 cm^{-1}) were taken from Ref. 6. (The corresponding values from the MP3/6-31G* calculation are 2222 and 628 cm^{-1}, 7.7% and 7.2% higher, respectively, similar in direction and magnitude of error to results on other molecules.) The result of the best fit is shown as the solid line in Fig. 2. The parameters obtained from the fit are listed in Table IV. The "anharmonicities" for the first and second band have been allowed to differ from zero. In such a complex polyatomic fit as this, the function of the "anharmonicity" is to absorb some of the consequences of the fact that the normal coordinates in the molecule and the ion may not be perfectly parallel, rather than to represent the conventional meaning of anharmonicity.

The $\hat{L}$ matrix entering into the computation of changes in bond distances involves a $\hat{G}$ matrix, which is known, and an $\hat{F}$ matrix. For the $\hat{F}$ matrix, the off-diagonal element has been taken to be zero, as in corresponding calculations for C_2N_2[21] and C_2H_2.[22] It has also been shown[6] that the off-diagonal element of the $\hat{F}$ matrix for neutral B_2O_2 is zero within the uncertainty and the calculated MP3/6-31G* off-diagonal element is small (-0.044 mdyn/Å) as well. The changes in bond distances obtained from the fitted parameters are listed in Table V, together with the results derived solely from ab initio calculations at various levels. While neither this complex fit nor the ab initio calculations can be expected to be precise, the general agreement between the two is encouraging. In most instances, the two approaches agree to within 0.01 Å. The largest discrepancies are for the changes in B–B distance on $(\pi_g)^{-1}$ and $(\sigma_g)^{-1}$. The B–B bond is much the softer of the two, and difficulties can be anticipated in both methods for establishing this distance accurately.

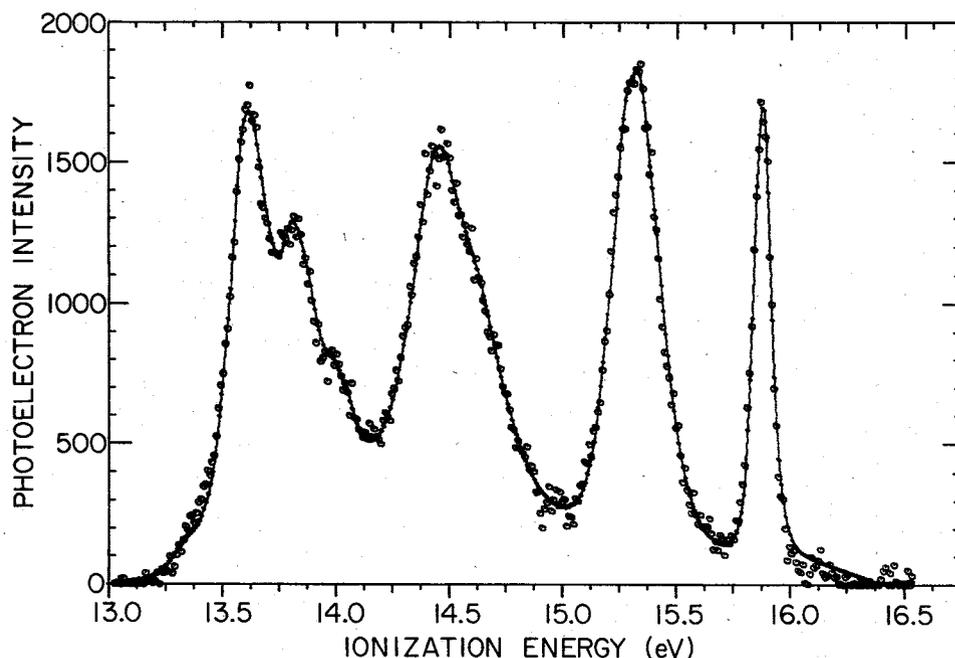

FIG. 2. Experimental spectrum of B_2O_2, with H_2O and linear background subtracted. O—Reduced experimental points. Smooth line—Least squares Franck–Condon fit to data. See the text for details of fitting procedure.

TABLE V. Bond distance changes accompanying ionization.

		$(\pi_g)^{-1}$	$(\pi_u)^{-1}$	$(\sigma_g)^{-1}$	$(\sigma_u)^{-1}$
A. From Franck–Condon fitting to experimental data					
I. Values of fitted parameters					
E_a (eV)		13.58	14.22	15.28	15.88
ω_1(cm^{-1})		1922	1714	2558	2087
x_1		0.05	0.07	0.00[e]	0.00[e]
ω_2(cm^{-1})		499	217	520	582
x_2		0.03	− 0.01	0.00[e]	0.00[e]
a_1		0.604	0.519	0.006	0.000
a_2		0.938	1.282	1.399	0.084
II. Derived changes in geometry[f]					
$\Delta r_{B-O}/\Delta r_{B-B}$(Å)	a	+ 0.050/ + 0.025 − 0.050/ − 0.025 + 0.027/ − 0.126 − 0.027/ + 0.126	+ 0.049/ + 0.041 − 0.049/ − 0.041 + 0.022/ − 0.135 − 0.022/ + 0.135	+ 0.010/ + 0.097 − 0.010/ − 0.097 + 0.018/ + 0.087 − 0.018/ − 0.087	+ 0.003/ + 0.023 − 0.003/ − 0.023 + 0.004/ + 0.022 − 0.004/ − 0.022
	b	+ 0.050/ + 0.033 − 0.050/ − 0.033 + 0.030/ − 0.136 − 0.030/ + 0.136	+ 0.043/ + 0.120 − 0.043/ − 0.120 + 0.036/ − 0.215 − 0.036/ + 0.215	+ 0.030/ + 0.112 − 0.030/ − 0.112 + 0.010/ + 0.103 − 0.010/ − 0.103	+ 0.003/ + 0.023 − 0.003/ − 0.023 + 0.004/ + 0.022 − 0.004/ − 0.022
B. From ab initio calculation (Δ SCF)					
$\Delta r_{B-O}/\Delta r_{B-B}$(Å)	c	+ 0.059/ − 0.016	+ 0.053/ + 0.062	+ 0.028/ + 0.051	+ 0.020/ + 0.023
	d	+ 0.040/ − 0.018	+ 0.039/ + 0.047	+ 0.022/ + 0.042	+ 0.013/ + 0.011
r_{B-O}/r_{B-B}(Å)	c	1.235/ 1.594	1.229/ 1.672	1.204/ 1.661	1.196/ 1.633
	d	1.236/ 1.613	1.235/ 1.678	1.218/ 1.673	1.209/ 1.642

[a]Using frequencies for the ground state of the molecule.
[b]Using fitted frequencies.
[c]STO-3G level.
[d]4-31G level.
[e]Anharmonicities for the third and fourth band have been fixed to zero.
[f]An ambiguity in sign ($\pm \Delta r$) results when using harmonic oscillator wave functions in a Franck–Condon fitting procedure. With two normal coordinates active, there are four possible solutions. In this instance, we have used chemical intuition (e.g., bonding vs nonbonding orbitals) to select one of these solutions, which is underlined.

V. CONCLUSIONS

A. Symmetry, structure, thermodynamic functions

Several arguments have been presented here, some based solely on *ab initio* calculations, others on experimental

TABLE VI. Thermodynamic functions of B_2O_2.[a]

T(K)	$-(F° − E_0°)/T$ (cal/deg mol)	$S°$ (cal/deg mol)
298.16	48.854	59.678
500	54.946	67.693
1000	64.634	79.847
1500	71.084	87.658
2000	75.977	93.404
2500	79.931	97.935
3000	83.253	101.670
3500	86.116	104.844
4000	88.633	107.602
4500	90.879	110.041
5000	92.906	112.225
5500	94.754	114.204
6000	96.451	116.012

$$H_{298} − H_0 = 3.228 \text{ kcal/mol}$$

[a]Isotopically averaged for boron isotopes. Symmetry number = 2 for all boron isotopic species, using the convention of W. F. Giauque and R. Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

observations, still others based on a comparison of calculated and experimental features which enable us to conclude that the most stable structure of B_2O_2 is linear symmetric O≡B–B≡O. In our judgment, the strongest arguments involve orbital sequences and ionization energies calculated for O≡B–B≡O and B–O–B–O, and compared with experiment. The best current estimates of the internuclear distances, 1.201 Å for the O≡B bond and 1.647 Å for the B–B bond, have been obtained in this work using a 6-31G* basis set and Møller–Plesset perturbation theory to third order. With this information and the experimentally deduced vibrational frequencies of Serebrennikov,[6] we have computed a revised set of thermodynamic functions $-(F° − E_0°)/T$, $S°$ and $H_{298}° − H_0°$, shown in Table VI. They differ significantly from the values in the JANAF tables,[23] not primarily because of geometry, but because of lower bending frequencies. The more recent Russian tabulation,[37] although still using estimated distances and some estimated frequencies, differs from the present results by 0.17 cal/deg -mol for $S°$ at 6000 K, and correspondingly less at lower temperatures.

B. Orbital ordering, nature of the orbitals and bonding

For C_2N_2, McLean and Yoshimine[24] performed an *ab initio* calculation very near to the Hartree–Fock limit. The

ordering of occupied orbitals they obtained (uppermost first) was $\pi_g, \pi_u, \sigma_g, \sigma_u$. Perhaps coincidentally, this is our preferred order for B_2O_2, although it is the wrong order for C_2N_2. For the latter, the experimentally deduced[20] ordering $\pi_g, \sigma_g, \sigma_u, \pi_u$ was confirmed only by inclusion of correlation carried out to third order perturbation theory.[25]

In the case of B_2O_2, the orbital ordering inferred from experiment, based on band shapes and areas, is in agreement with the Hartree–Fock calculation. The π_g orbital is predicted to be B–O bonding, and the primary effect of ionization from this orbital is seen to be an increase in B–O distance, both from SCF calculation of the $(\pi_g)^{-1}$ state and Franck–Condon fitting of the $(\pi_g)^{-1}$ band. The π_u orbital is predicted to be bonding in both B–O and B–B bonds, again borne out by calculation and Franck–Condon fitting of the $(\pi_u)^{-1}$ band. The $(\sigma_u)^{-1}$ state is predicted to have a geometry very close to that of the neutral B_2O_2, and indeed the width of this band is almost our resolution limit, consistent with Franck–Condon transitions which primarily maintain vibrational quantum numbers. Hence, the ordering of orbitals in B_2O_2 appears to conform to the Hartree–Fock predictions, but it would be interesting to see the effects of higher order perturbation theory on the energies.

In the $(\pi_g)^{-1}$ and $(\pi_u)^{-1}$ states of B_2O_2 and C_2N_2 the possibility exists for Renner–Teller splitting. It is difficult to discern evidence for this in our Boltzmann-broadened peaks, but surprisingly we have found no discussion of this possibility for C_2N_2.

It is instructive to examine the bond strengths in cyanogen and B_2O_2, both in light of the above discussion and with reference to the conventional structures written for these species. The total energy of atomization[26] is very nearly the same: 21.34 eV for B_2O_2, 21.32 eV for C_2N_2. A rough measure of the C–C bond strength in C_2N_2 is obtained by calculating the dissociation into 2 CN. The value[26] obtained (5.97 eV) is very nearly the dissociation energy[27] of C_2, 6.11 eV. In B_2O_2, the scission into 2 BO requires[26] 4.73 eV, compared[27] to $D_0(B_2) = 2.97$ eV. Hence, the nominal single bond in B_2 has become significantly stronger in OB–BO.

The nominal double bond (O=B) estimated[26] in this fashion is 8.30 eV, larger than the nominal triple bond in N≡C.

APPENDIX. THE FRANCK–CONDON FITTING PROCEDURE

The photoelectron spectrum contains information about the change in geometrical structure upon ionization. This information can be extracted by quantitative application of the Franck–Condon principle. In the usual formulation of the Franck–Condon principle, the electronic transition moment R_e is assumed to be constant for a given photoelectron band. The vibrational intensity distribution is given by the square of the associated transition moment M:

$$M = R_e \int \psi'^*(Q')\psi''(Q'')dQ',$$

where Q', Q'' are normal coordinates and ψ' and ψ'' are the vibrational wave functions of the ion and the molecule, respectively. If there are n normal modes of vibration, the vibrational wave function of each state can be represented as

$$\psi = \prod_{i=1}^{n} \phi_i(Q_i),$$

while the Duschinsky transformation[28] describes the change in normal coordinates

$$Q_i'' = \sum_j a_{ij}Q_j' + d_i, \quad i = 1,2,...n,$$

where d_i is the shift of the equilibrium position in normal coordinate space.

If the normal coordinates Q' and Q'' are assumed to remain parallel to each other, the simplified transformation of Coon et al.[29]:

$$Q_i'' = Q_i' + d_i, \quad i = 1,2,...n$$

is obtained. If one takes ϕ_i' and ϕ_i'' as harmonic oscillator wave functions centered about their respective equilibrium positions, with frequencies ω_i' and ω_i'', the relative transition probabilities are given as

$$P_{m,0,...,x \to n,p,...,y} = |R_e|^2(P_{m \to n})(P_{0 \to p})...(P_{x \to y}),$$

where $m,0,...,x$ and $n,p,...,y$ are the vibrational quantum numbers of the molecule and ion, respectively. The one-dimensional probability $P_{m \to n}$ was evaluated by several authors[30–33]. It can be expressed as

$$P_{m \to n} = e^{-a(1 - \lambda_2/\lambda_1)} \left\{ \sum_{\mu=0}^{m} \sum_{\nu=0}^{n} \right.$$
$$\left. \times \left[\frac{1}{\mu!}\binom{m}{\mu}\frac{1}{\nu!}\binom{n}{\nu} \right]^{1/2} \alpha^\mu \beta^\nu \langle m - \mu | m - \nu \rangle \right\}^2,$$

$$\lambda_1 = \frac{1}{2}\frac{\omega' + \omega''}{\sqrt{\omega'\omega''}},$$

$$\lambda_2 = \frac{1}{2}\frac{\omega' - \omega''}{\sqrt{\omega'\omega''}},$$

$$\alpha = -\sqrt{a}/\lambda_1,$$

$$\beta = \sqrt{a}(1 - \lambda_2/\lambda_1).$$

The notation follows closely that of Ref. 33, and the expression can be derived from their equations. The overlaps $\langle m - \mu | n - \nu \rangle$ can be evaluated using the recursion relations:

$$\langle o | o \rangle = 1/\lambda_1^{1/2},$$

$$\langle m | n + 1 \rangle = [m/(n+1)]^{1/2}(1/\lambda_1)\langle m - 1 | n \rangle$$
$$+ [n/(n+1)]^{1/2}(\lambda_2/\lambda_1)\langle m | n - 1 \rangle,$$

$$\langle m + 1 | n \rangle = [n/(m+1)]^{1/2}(1/\lambda_1)\langle m | n - 1 \rangle$$
$$- [m/(m+1)]^{1/2}(\lambda_2/\lambda_1)\langle m - 1 | n \rangle.$$

For the case $\omega'' = \omega'$, $P_{m \to n}$ reduces to

$$P_{m \to n} = e^{-a}\left\{\frac{a^{m+n}}{m!n!}\right.$$
$$\left. \times \sum_{l=0}^{\min(m,n)} \frac{m!n!}{l!(m-l)!(n-l)!}\frac{1}{(-a)^l}\right\}^2,$$

which, in turn, for the case $m = 0$ reduces to the familiar Poisson distribution

$$P_{0 \to m} = e^{-a} \frac{a^n}{n!}.$$

The present fitting procedure used the more general expression for the case $\omega'' \neq \omega'$, and explicitly included the change in vibrational excitation only for the two totally symmetric vibrations. (Note that the procedure implicitly includes all other Boltzmann-populated vibrations as well, assuming that the frequencies of these vibrations do not change upon ionization and that the coupling parameter $a = 0$.) The instrumental resolution has been incorporated by using a Gaussian for each transition whose half-width is the experimental resolution (FWHM) and whose height is proportional to the calculated probability. The hot bands have been included by convoluting the calculation with a Boltzmann distribution. The parameters entering the fit were the experimental resolution, temperature, and the totally symmetric vibrational frequencies of the neutral molecule. The parameters to be determined by the fit were (for each band) the two totally symmetric frequencies, with the corresponding anharmonicities (optional), the corresponding coupling parameters a, the adiabatic ionization energy and a scaling factor. The optional anharmonicity only affected the energy scale, not the overlaps. The least-squares fit was pursued using a method[34] that does not require a calculation of derivatives. Only one band was fitted at a time, using the others as a background. This was repeated in sequence for each band until self-consistency was reached.

If one defines a column matrix $\hat{K}$ such that its elements K_i are given by

$$K_i = \pm \left[\frac{a}{\omega'} \right]^{1/2}$$

the change in symmetry coordinates will be defined by the column matrix $\hat{S}$ through

$$\hat{S} = \sqrt{2h} / \sqrt{2\pi c} \, \hat{L} \hat{K}.$$

Note that the computed change in symmetry coordinates depends on the (arbitrary) choice of signs for K_i.

The $\hat{L}$ matrix is connected to the kinematic matrix $\hat{G}$ and the force constant matrix $\hat{F}$ through

$$\hat{L} \hat{L}^\dagger = \hat{G},$$
$$\hat{G} \hat{F} \hat{L} = \hat{\Lambda} \hat{L},$$

where the eigenvalues Λ_i of GF are given as

$$\Lambda_i = 4\pi^2 c^2 (\omega_i')^2.$$

The form of the $\hat{G}$ matrix depends on the choice of the symmetry coordinates, and is evaluated through standard methods.[35] Knowing the frequencies of vibrations in the ion, and keeping the off-diagonal elements of the $\hat{F}$ matrix equal to zero, both the $\hat{F}$ and the $\hat{L}$ matrix can be evaluated. However, in such a fitting procedure (especially if bands overlap and do not show well resolved structure) the obtained frequencies ω' have much less weight than the coupling parameters a.[36] Therefore, an alternative approach is to use the force constant matrix for the ground state of the molecule together with the ground state frequencies. In most cases the difference between answers based on different choices of the $\hat{F}$ matrix is well within the experimental uncertainty.

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