Observation of the Second Triplet of Solid Benzene Using NO Perturbation

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Notes

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As mentioned in our previous paper on the first and second triplets of solid benzene,[1] the absorptions observed in the 37 000-cm^{-1} region under O_2 perturbation could conceivably be "due to the benzene–O_2 'double' transition $[{}^3B_{1u}\ {}^1\Delta_g]\leftarrow[{}^1A_{1g}\ {}^3\Sigma_g^-]$." To eliminate this possibility, benzene–NO mixed crystals have been grown and their spectra taken. The mixed crystals were prepared in the following manner: The benzene was purified as before and checked for purity by taking its spectrum. No impurity absorptions in the 37 000-cm^{-1} region were observed in 2-cm-thick crystals at 4.2°K. The NO was purified by a series of vacuum sublimations until the originally multicolored solid was white. NO, thus purified and placed in a hydrocarbon glass at 77°K, shows no absorption in the 37 000-cm^{-1} region. However, in the 40 000-cm^{-1} region a strong cutoff was observed, believed to be caused by the γ bands of NO, indicating that NO had dissolved in the glass.

Several NO–benzene mixed crystals were prepared by loading a sample cell containing purified benzene with 10^{-1} to 10^{-2} liter·atm of the purified NO gas. Crystals were grown by lowering the cell at the rate of 1 mm/h through a temperature gradient of about 100°C/cm (10° to ~-100°C), and then directly into liquid N_2. This technique gives excellent pure benzene crystals but the mixed crystals were highly cracked. The mixed crystals containing large amounts of NO were so cracked that only the (0–0) band of the first triplet absorption system could be seen. However, the crystals more dilute in NO were sufficiently less scattering to be investigated in the 37 000-cm^{-1} region.

New absorptions are observed at 36 983±50 and 37 324±50 cm^{-1}. These are assigned to the second triplet transition $({}^3E_{1u}\leftarrow{}^1A_{1g})$ of the perturbed solid benzene system. The reason for the difference between the energy of these absorptions and those observed under O_2 perturbation (36 560±50 and 37 170±50 cm^{-1}) is not obvious. It does not appear to be large enough to justify a new interpretation. It therefore seems improbable that the absorptions observed in the O_2-perturbed system are due to a benzene–O_2 "double" transition. The absorptions both in the benzene–O_2 and the benzene–NO systems in the 37 000-cm^{-1} region are, as concluded earlier,[1] most likely caused by the perturbed second triplet of benzene.

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[*] Supported in part by the U.S. Atomic Energy Commission.

[†] Contribution No. 3395.

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Variational Group-Function Calculation of Atomic Excited States*

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We wish to report, in this Note, a variational "group-function" (GF) calculation on an excited state of the beryllium isoelectronic sequence. The ground state of this sequence has been investigated

TABLE I. Calculations on the $1s^22p^2(^1D)$ states of the beryllium isoelectronic sequence (atomic units throughout).

Z	One-detor energy	"Split-shells" energy	Exptl energy	Calc correlation	Exptl correlation	$2p^2$ correlation
4	−14.27641	−14.31955	−14.41199	0.04314	0.13558	0.01783
5	−23.74801	−23.79354	−23.88770	0.04553	0.13969	0.02065
6	−35.73060	−35.77819	−35.88209	0.04759	0.15149	0.02298
7	−50.21953	−50.26863	−50.38667	0.04910	0.16714	0.02477

using this method, and results in good general agreement with experiment are obtained.[1] The $1s^22p^2$ (^1D) state of this sequence seems well suited to the GF approach consisting of two shells of "doubly occupied orbitals" which are weakly interpenetrating. Hence, intrashell correlation is expected to be strong and intershell correlation, neglected in the simple GF approach, should be quite weak.

We have calculated the total energy of the $1s^22p^2$ (^1D) state of the beryllium isoelectronic sequence using a wavefunction of the form

$$\Phi(1,2,3,4)=M\mathfrak{A}\Phi_{Aa}(1,2)\Phi_{Bb}(3,4), \qquad (1)$$

characteristic of the GF method. Both groups were described by "split-shell" wavefunctions, using Slater-type orbitals (STO's) $1s$, $1s'$, $2p$, $2p'$:

$$\Phi_{Aa}(1,2)=[1/2(1+S_1^2)^{\frac{1}{2}}]\{1s(r_1)1s'(r_2)$$
$$+1s(r_2)1s'(r_1)\}[\alpha(s_1)\beta(s_2)-\alpha(s_2)\beta(s_1)],$$
$$\Phi_{Bb}(3,4)=[1/2(1+S_2^2)^{\frac{1}{2}}]\{2p(r_3)2p'(r_4)$$
$$+2p(r_4)2p'(r_3)\}[\alpha(s_3)\beta(s_4)-\alpha(s_4)\beta(s_3)], \qquad (2)$$
$$S_1=\langle 1s\mid 1s'\rangle, \qquad S_2=\langle 2p\mid 2p'\rangle.$$

The split-shell functions include only radial intrashell correlation. We evaluated the matrix elements of the operators in the nonrelativistic Hamiltonian for the four-electron atom by standard methods.[2]

The $1s^22p^2$ (^1D) state is the lowest state of ^1D symmetry so that the application of the variation method is straightforward, the orbital exponents of the four STO's being the variational parameters. The results of the calculation are collected in Table I.

The expectation value of the Hamiltonian over a single determinant of (optimized) STO's has been used as a standard of reference for the calculation of correlation energies, since no Hartree–Fock wavefunction is available for this state. We have not estimated the nonrelativistic eigenvalues for the state involved as the "ionization-potential-correction" method, used earlier,[2] is inappropriate for two electrons in the same shell. Thus, the column labeled "Experimental correlation" in Table I in fact contains the relativistic corrections which are not negligible for $Z>5$. In the last column of Table I we give the difference between the calculated radial correlation energies for the $1s^22p^2$ (^1D) state and the $1s^2$ state of the ion with the same nuclear charge. These figures give an estimate of the calculated radial correlation energy in the $2p^2$ shell (i.e., assuming that the intrashell correlation of the $1s^2$ pair is independent of the addition of outer electrons[3]). The optimized wavefunction parameters are collected in Table II.

The results show that intrashell radial correlation calculated in this way accounts for about 30% of the observed correlation energy.

If we add to the calculated radial correlation energy the calculated angular correlation energy of the isolated $1s^2$ ion (see Table IV of Ref. 2) this makes the correlation energy about 47% of that observed. Since intershell correlation may be safely assumed to be quite small, the remaining energy must be largely intrashell angular correlation in the $2p^2$ shell.

TABLE II. Optimum orbital parameters for the $1s^22p^2(^1D)$ states.

Z	ζ_{1s}	$\zeta_{1s'}$	ζ_{2p}	$\zeta_{2p'}$
4	4.949	3.332	1.286	0.650
5	5.523	3.879	1.756	1.044
6	7.191	5.205	2.545	1.641
7	8.023	5.945	3.043	2.054

There are other states of this isoelectronic sequence of ^1D symmetry very close (<0.03 a.u. for Be) in energy to the $1s^22p^2(^1D)$ state, namely the $1s^22s\,nd(^1D)$ ($n=3$–6) state, and inclusion of these configurations as "excited states" of the $2p^2$ shell is expected to account for a large part of the angular-correlation energy.

An interesting feature of the optimized-wavefunction parameters is the strong deshielding effect of one-half of the split shell on the other, the orbital exponent of one of the $1s$ STO's being $>Z$.

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[*] A pilot calculation of the type described here has been reported by N. G. Mukherjee, N. K. Dasgupta, and M. A. Ali [Indian J. Pure Appl. Phys. **3**, 402 (1965)] but full minimization of all parameters was not carried through due to lack of automatic computing facilities.

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[3] See Ref. 2 for a discussion of this point.