Research Laboratory, and the University of Illinois, and IBM 7040 time granted by the University of Arkansas. We also thank Dr. R. Wolfgang, Dr. F. S. Rowland, and Dr. B. C. Musgrave for helpful discussions and Mr. Sinan Kunt for assistance with some of the calculations.

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See the reviews by R. Wolfgang in Ann. Rev. Phys. Chem. 16, 15 (1965) and in Progr. Reaction Kinetics 3, 97 (1965), and references contained therein.

2 R. N. Porter, R. D. Sharma, and M. Karplus (to be published).
3 A. Kuppermann and J. M. White, J. Chem. Phys. 44, 4352 (1966). Their value for $E_1$ is 0.33±0.02 eV in comparison with the calculated value 0.26 eV for a molecular temperature of 300K (see Footnote 3).
5 Details concerning the reaction mechanism, including a differentiation between displacement and abstraction contributions as a function of energy, can be obtained from an analysis of the collision trajectories (to be published).
9 Furthermore, preliminary statistical calculations (Refs. 11 and 12) of relative yields $Y$, using both "hard-sphere" and "soft-sphere" moderator models for equimolar mixtures of H$_2$ and D$_2$ and varying moderator (He) concentrations, extrapolate to a $Y_{HT}/Y_{PT}$ value of 1.37 for unit He mole fraction at 300K with the $S(V,\phi)$ values reported here.
11 R. N. Porter and S. Kunt (to be published).

Notes

Observation of the Second Triplet of Solid Benzene Using NO Perturbation*

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(Received 14 July 1966)

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 $[{\beta}_{1u} \Delta_{1g} - [{\beta}_{1u} \Sigma_{1g} + 2 \Sigma_{1g}^-]$." 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 4.2K. 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 77K 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 $\gamma$ 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$^{-3}$ to 10$^{-4}$ 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 $\sim$100°C), and then directly into liquid N$_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 $(E_{1u} - A_{1u})$ 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.

The support and encouragement from Professor G. W. Robinson is gratefully acknowledged by the authors.

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† Contribution No. 3395.

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
using this method, and results in good general agreement with experiment are obtained. The 1s²2p² (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 1s²2p² (1D) state of the beryllium isoelectronic sequence using a wavefunction of the form

\[
\Phi(1, 2, 3, 4) = M_{\alpha} \Phi_{\alpha\alpha}(1, 2) \Phi_{\beta\beta}(3, 4),
\]

characteristic of the GF method. Both groups were described by "split-shell" wavefunctions, using Slater-type orbitals (STO's) being the variational parameters. The results of the calculation are collected in Table I. 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 1s² 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 2p² shell.

There are other states of this isoelectronic sequence of 1D symmetry very close (\(<0.03\) a.u. for Be) in energy to the 1s²2p² (1D) state, namely the 1s²2s nD (n=3–6) state, and inclusion of these configurations as "excited states" of the 2p² 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.

* 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.


See Ref. 2 for a discussion of this point.

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### Table I. Calculations on the 1s²2p² (1D) states of the beryllium isoelectronic sequence (atomic units throughout).

<table>
<thead>
<tr>
<th>Z</th>
<th>One-detor energy</th>
<th>&quot;Split-shells&quot; energy</th>
<th>Exptl energy</th>
<th>Correlation energy</th>
<th>Exptl correlation</th>
<th>2p² correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-14.27641</td>
<td>-14.31955</td>
<td>-14.41199</td>
<td>0.04314</td>
<td>0.13558</td>
<td>0.01783</td>
</tr>
<tr>
<td>5</td>
<td>-23.74801</td>
<td>-23.79354</td>
<td>-23.88770</td>
<td>0.04553</td>
<td>0.13969</td>
<td>0.02065</td>
</tr>
<tr>
<td>6</td>
<td>-35.73060</td>
<td>-35.77819</td>
<td>-35.88209</td>
<td>0.04759</td>
<td>0.15149</td>
<td>0.02298</td>
</tr>
<tr>
<td>7</td>
<td>-50.21953</td>
<td>-50.26863</td>
<td>-50.38667</td>
<td>0.04910</td>
<td>0.16714</td>
<td>0.02477</td>
</tr>
</tbody>
</table>

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### Table II. Optimum orbital parameters for the 1s²2p² (1D) states.

<table>
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<tr>
<th>Z</th>
<th>(\xi_1)</th>
<th>(\xi_1')</th>
<th>(\xi_2)</th>
<th>(\xi_2')</th>
</tr>
</thead>
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<tr>
<td>4</td>
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<td>3.332</td>
<td>1.286</td>
<td>0.650</td>
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<tr>
<td>5</td>
<td>5.523</td>
<td>3.879</td>
<td>1.756</td>
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<tr>
<td>6</td>
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<td>5.205</td>
<td>2.545</td>
<td>1.641</td>
</tr>
<tr>
<td>7</td>
<td>8.023</td>
<td>5.945</td>
<td>3.043</td>
<td>2.054</td>
</tr>
</tbody>
</table>