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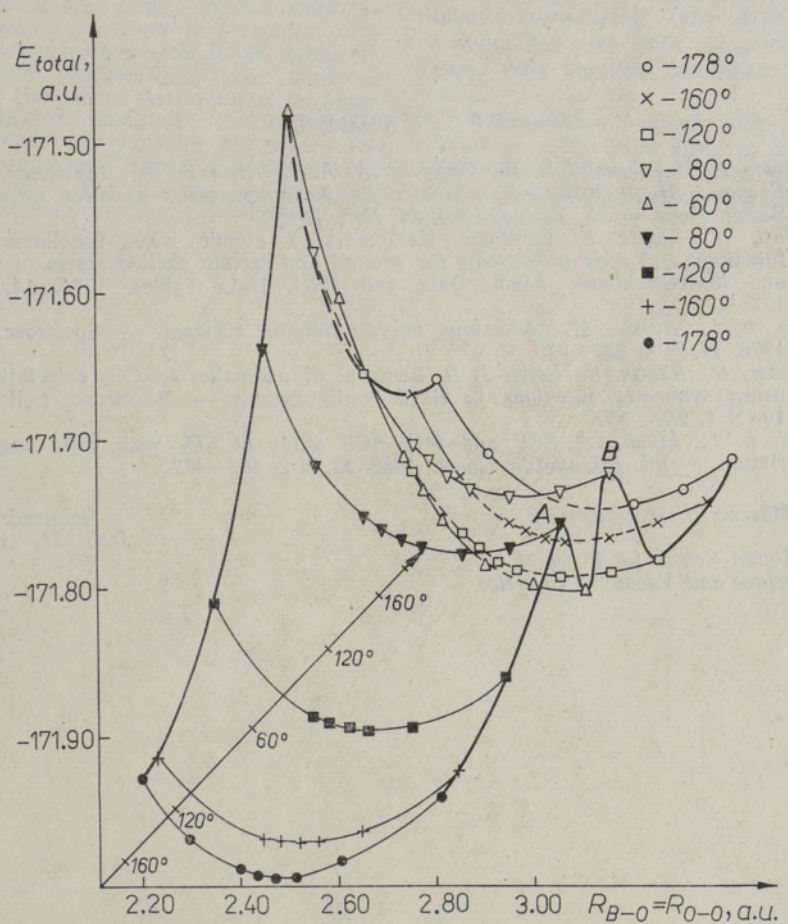
THEORETICAL INVESTIGATION OF THE O—B—O → B—O—O REARRANGEMENT

P.-E. LOMP, V. SIMKIN, A. DEMENTJEV, N. STEPANOV. O—B—O→B—O—O ÜMBERASETUSE TEOREETILINE UURIMINE

П.-Э. ЛОМП, В. СИМКИН, А. ДЕМЕНТЬЕВ, Н. СТЕПАНОВ. ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ПЕРЕГРУППИРОВКИ O—B—O → B—O—O

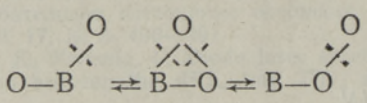
(Presented by M. Veiderma)

To investigate the O—B—O → B—O—O rearrangement, *ab initio* restricted SCF calculations of fragments of potential surfaces in C_s point



Potential surface of O—B—O→B—O—O rearrangement. SCF calculations in C_s point group in STO-3G basis set.

group for $X_2\Pi$ ($^2A'$) and $^2A''$ states using the SPUSH program system [1] were carried out (R_{B-O} and R_{O-O} here varied between 2.00 and 3.20 a. u., bond angle between 180 and 60°). The calculations in the standard STO-3G basis set [2] yield OBO to be more stable. The rearrangement is proposed to go over a triangular structure:



The potential surface of this rearrangement for the ground state is presented in the Figure. The surface for the $^2A''$ state is similar.

It is remarkable that the total energy minimum corresponds to approximately $R_{B-O}=R_{O-O}$ in BOO. This condition is also used in the Figure.

The calculations show an existence of peaks approximately at 80° (A and B). So the triangular structure seems to have a stability. Similar results have been published for $X^1\Sigma^+$ ($^1A_1$) state of CO_2 [3, 4] where the second minimum was found at $\angle OCO=80°$ and maximum at 105° while MCSCF treatment [5] between 60 and 180° showed that a cyclic isomer is unstable.

For the energy of rearrangement a value of 320 kJ/mol (0.136 a. u.) has been found.

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