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Pump-probe spectroscopy of Rg-Br₂ linear isomers¹ JORDAN PIO, CRAIG BIELER, WYTZE VAN DER VEER, KENNETH JANDA, University of California-Irvine — We have recorded and analyzed the $X \rightarrow B$ spectra for three Rg-Br-Br linear isomers [Rg = He, Ne, Ar] using pump-probe spectroscopy. This work is an interesting test case for the transition from quantum to quasi-classical dynamics, and how the dynamics are interconnected with changes in the potential energy surface. Helium is not only much lighter than argon, but the He-Br₂ potential well is much shallower than that of Ar-Br₂. Excitation spectra to individual Rg-Br₂ (B, ν') intermolecular potentials were recorded by probing the Br₂ (B, ν') asymptotic limit of the potential while scanning the pump laser. The continuum spectra of the three species are very different, with the He-Br₂ spectrum peaking at threshold while the Ar-Br₂ spectrum is negligible at threshold and strongly blue shifted. The linear Ne-Br₂ bond energy was measured to be $71 \pm 3 \text{ cm}^{-1}$ by the threshold energy for the onset of the continuum. Since excitation tends to move electron density to the σ^* orbital of the Br-Br bond near the rare gas atom, the intramolecular stretching vibration (Br-Br) and the intermolecular stretching vibration (Rg-Br) are strongly coupled. The experiments will be compared to a two dimensional model using the best available potential energy functions.

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