Supplementary Material of

The dynamics of the Hg + Br₂ reaction.

Elucidation of the reaction mechanism for Br exchange reaction

P. G. Jambrina,†,‡ M. Menéndez,† and F. J. Aoiz*,†

†Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain.

‡Present Addresss: Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, Madrid, Spain.

E-mail: aoiz@ucm.es
The striking difference between measured and theoretically simulated LAB ADs for Hg+I$_2$ and Hg+Br$_2$, respectively, calls for a stringent test to assure the reliability of the simulation carried out in this work. Therefore, to test whether a backward angular distribution could give rise to the experimental LAB AD, we have carried out a simulation using a DCS which is the specular image of that obtained in the actual calculation, that is, inverting the CM TAV-DCS such that the intensity at an angle $\theta$ becomes $180^\circ - \theta$. The resulting CM distribution is thus dominated by backward scattering, as can be seen in Fig. S1. For this concocted DCS, sideways and backward scattering become essentially disentangled, as can be seen in the bottom panel of Fig. S1, and the simulated LAB AD is characterized by three peaks, two small ones at $\Theta = 60^\circ$ and $105^\circ$ due to CM sideways scattering and a large peak at $85^\circ$ due to backward scattering. Leaving aside for the moment the two smaller peaks, and bearing in mind the obvious kinematic differences in the collisions of Br$_2$ and I$_2$, leaving aside for the moment the two smaller peaks, and bearing in mind the obvious kinematic differences in the collisions of Br$_2$ and I$_2$,

![Newton diagram](image1)

**Fig. S1** Top panel: Newton diagram for the Hg+Br$_2$ reaction showing a fictitious angle-velocity polar map which is a specular image of that obtained in the actual calculations shown in Fig. 9 of the main text. With this TAV-DCS, backward scattering is predominant and apart from the peaks due to sideways scattering, the LAB AD, shown in the bottom panel, resembles that measured for the Hg+I$_2$ reaction.
the resulting LAB AD is similar to those experimentally obtained for the Hg+I\textsubscript{2} at similar energies. Moreover, the absence of the lateral peaks in the Hg+I\textsubscript{2} LAB ADs clearly indicates that sideways scattering is almost negligible in this reaction, in contrast with the theoretical results obtained for Hg+Br\textsubscript{2}. Therefore, it can be concluded that at high energies the dynamics predicted for Hg + Br\textsubscript{2} is significantly different than that experimentally deduced for the Hg+I\textsubscript{2} reaction. Moreover, the results obtained with QCT calculations on the same PES simply changing the mass of Br to that of iodine also show a predominance for forward scattering. Figure S2 depicts the comparison of the respective DCSs at 3.5 eV collision energy. Although forward peak is less prominent and sideways scattering somewhat more relevant, there is no indication of backward scattering as that found in the experimental study. Therefore, a simple kinematic effect, as that changing the isotopic mass, cannot account for the important discrepancy between the theoretical results for Hg+Br\textsubscript{2} and the measured DCS for Hg+I\textsubscript{2}.

Simulations of LAB ADs have been also performed under experimental conditions in which the two crossed molecular have similar velocities, such that centroid (the center of the Newton sphere given by the tip of the velocity of the CM) lies close to $\Theta_{\text{LAB}} = 45^\circ$. The resulting LAB AD and related Newton triangle are depicted in Fig. S3. The use of this kinematic arrangement
has the advantage of allowing the almost complete separation of forward, sideways and backward scattering in three different angular ranges. As it could be expected, the LAB AD is dominated by a sharp peak centered at 25° due to the prevailing CM forward scattering. The rest of the angular distribution is mainly due sideways scattering, covering the 30–60° angular range.

Fig. S3 Left panel: Newton diagram for the Hg+Br₂ reaction under a kinematic arrangement with two seeded molecular beams, such that the velocities in the LAB frame of Hg and Br₂ are similar. The right panel depicts the resulting LAB AD with the contributions from the various ranges of CM scattering angles.

Fig. S4 Cross Section as a function of the angle between the Br–Br internuclear axis and the relative velocity, $\theta_r$, at the beginning of the trajectory and the impact parameter for the Hg + Br₂ → HgBr + Br reaction at the indicated collision energies.
The correlation between the initial angle of attack and the impact parameter is shown in Fig. S4 at four collision energies. From the inspection of the figure, it becomes evident that (i) collinear collisions do not contribute to the reaction; (ii) only at the lowest energies, the preferred approach is centred around $90^\circ$; (iii) for $E_{\text{coll}} \geq 2.3$ eV, reactive collisions take place at skewed angles.