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Quasi-Quantum Treatment of the rotationally inelastic NO-He scattering

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Synopsis An analytical scaling relationship is presented that describes the collision energy dependence of rotationally inelastic differential cross sections and allows separation of kinematic and potential-energy effects.

The Quasi-Quantum Treatment (QQT) of rotationally inelastic scattering employs the Feynman path integration over angular variables in the kinematic apse frame, which replace the traditional partial wave expansion approach, provides a physically compelling framework while requiring much less computational effort.

An analytical scaling rule based on the QQT method presents a general relationship for the disposition of kinetic energy and rotational energy in one of the most fundamental quantities of inelastic scattering, the differential cross section (DCS). We show that scaling rules, strictly applicable in the limiting case of a hard shell potential but approximately true in a wide range of scattering problems, imply that the angular distribution at low collision energy maps onto a smaller angular range of the DCS at higher collision energy. This mapping provides an intuitively link between incoming kinetic energy and exit scattering angle.

Specifically, we consider the collision energy dependence of the rotationally inelastic DCS associated with atom-diatom scattering processes. Within a quasi-quantum treatment, we derive a series of analytic expressions that rigorously describe this collision energy dependence, and we show that these relationships hold well for the rigorously calculated quantum chemical DCSs. In the case of NO(X)+He, the DCSs at a collision energy of $E_{col}^L = 63\text{meV}$ can be accurately reconstructed from the corresponding NO(X)+He DCSs at $E_{col}^H = 147\text{meV}$. This implies that there is no need to carry out addition expensive close-coupled calculations to obtain DCSs at collision energies between $E_{col}^L = 63\text{meV}$ and $E_{col}^H = 147\text{meV}$.

While the scaling rule applies almost exactly to full quantum calculations performed on the NO(X)+He system, this will not necessarily be the case for all systems. Discrepancies between the energy scaling of the full QM DCSs and the analytic

formalism presented here directly reveal the relative importance of the repulsive, hard-shell like part of the potential compared to the softer, longer range components. Furthermore, the scaling formalism allows explicit analysis of the angular range of a DCS that will be of importance in determining the same DCSs at a different collision energy. This allows the designation of particular (energy dependent) scattering angle ranges which can be associated with specific features of a state of the art ab initio PES. This viewpoint provides a novel tool with which to optimize the accuracy of an ab initio atom-diatom PES, and is in particular applicable to the repulsive features of the potential, which are often the most challenging to accurately determine. Such enhancement in the accuracy of ab initio PESs would be of interest to the whole field of chemistry.

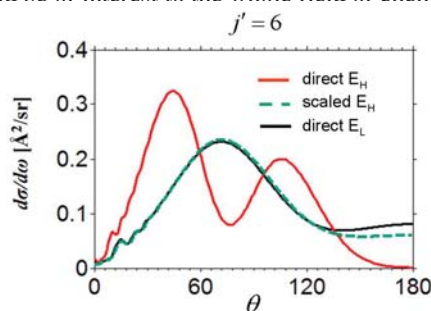


Figure 1. Rotationally inelastic QM DCS's of He-NO transitions at a collision energy $E_{col}^H = 147\text{meV}$ (red solid line) and $E_{col}^L = 63\text{meV}$ (black solid line) are shown. DCS's at $E_{col}^H = 147\text{meV}$ scaled (green dot line) by the QQT method fits nearly perfect with that direct calculated one at $E_{col}^L = 63\text{meV}$.

References

- [1] X. Zhang, C. J. Eyles, C. A. Taatjes, D. Ding and S. Stolte. 2013, Phys. Chem. Chem. Phys., 15, 5620

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