$D_2(v = 1, j = 0)$ in collisions with Ar atoms [31] are presented over an energy range of $10^{-8} - 10^{3}$ cm^{-1}. The cross sections exhibit a curvature characteristic of a resonant enhancement in the energy range $10^{-5} - 10^{-3}$ cm^{-1}. Such enhancement of the cross section can occur when the interaction potential supports a virtual state or a very weakly bound state near the channel threshold leading to a zero-energy resonance. The virtual state is characterized by a large negative scattering length while the bound state is characterized by a large positive scattering length. For the present case the real part of the scattering length is large and positive ($\alpha_{10} = 97.0$ Å) and the resonance occurs from the decay of a loosely bound van der Waals complex supported by the entrance channel potential. For energies below 10^{-2} cm^{-1} the cross section is dominated by s-wave scattering in the incident channel and the zero-energy resonance arises from s-wave scattering in the entrance channel.

The resonant enhancement is more clearly seen in the plot of the reaction probability as a function of the kinetic energy shown in Fig. 3. The probability peaks at an energy of 6.0×10^{-4} cm^{-1} which roughly corresponds to the binding energy of the quasibound state. The resonance appears in the scattering calculations at energies above the threshold due to its close proximity to the channel threshold. The binding energy of the quasibound state can be estimated using the scattering length approximation [10, 31]. The magnitude of the binding energy is given by $|E_b| = \hbar^2 \cos 2\gamma_{10}/(2\mu|a_{10}|^2)$ where μ is the reduced mass of the Ar$-$D$_2$ system, $a_{10} = \alpha_{10} - i\beta_{10}$ is the scattering length for the $v = 1, j = 0$ level, and $\gamma_{10} = \tan^{-1}(\beta_{10}/\alpha_{10})$. This yields a value of $|E_b| = 4.9 \times 10^{-4}$ cm^{-1}, in reasonable agreement with the exact value derived from scattering calculations.

A more accurate value of the binding energy can be obtained using the effective range formula given by Forrey et al. [20]:

$$|E_b| = \frac{\hbar^2}{\mu r_0^2}\left(1 - \frac{\alpha_{10} r_0}{|a_{10}|^2} - \sqrt{1 - \frac{2\alpha_{10} r_0}{|a_{10}|^2}}\right)$$

where r_0 is the effective range of the potential which may be evaluated by fitting the low energy behavior of the phase shift for the elastic channel to the standard effective range formula, $k_{10} \cot \delta_{10} = -1/\alpha_{10} + r_0 k_{10}^2/2$. For Ar$-D_2(v = 1, j = 0)$ collisions, the effective range formula yields $r_0 = 16.32$ Å. The resonance position calculated using the effective range approximation is $|E_b| = 5.95 \times 10^{-4}$ cm^{-1}, in excellent agreement with the value of 6.0×10^{-4} cm^{-1} obtained from the scattering calculations. It is generally very difficult to accurately evaluate energies of such weakly bound states using standard bound state codes and the effective range formula provides a convenient and reliable method to calculate binding energies of weakly bound states that lead to zero-energy resonances.

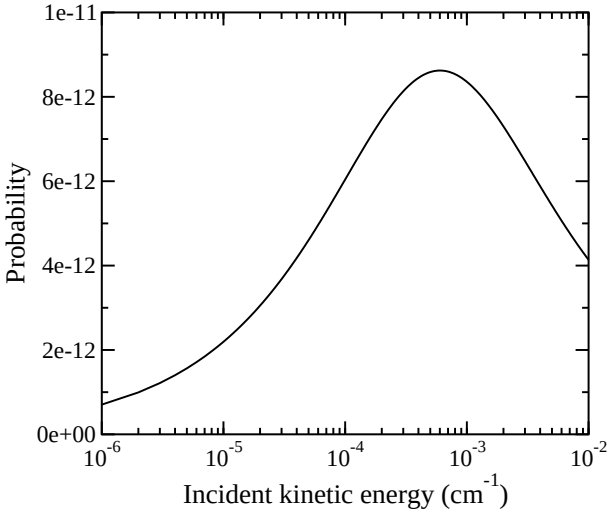

FIG. 3: Total probability of quenching of the $v = 1, j = 0$ level of D_2 in collisions with Ar atoms as a function of the incident kinetic energy. The peak value of the probability corresponds to a zero energy resonance. Reproduced with permission from Uudus et al. [31].

One of the challenging aspects of cold and ultracold collisions is the sensitivity to details of the interaction potential. Even the best available methods for the electronic structure calculations of PESs result in errors much larger than the collision energies in the cold and ultracold regime and the dynamics calculations are often sensitive to small changes in the interaction potential. To explore the sensitivity of cold and ultracold collisions to details of the interaction potential, Lee et al. [32] performed a comparative study of the ultracold collision dynamics of the He$-$H$_2$ system using the MR potential and a more recent ab initio potential developed by Boothroyd, Martin and Peterson (BMP) [33]. The BMP potential was considered to be an improvement, approaching chemical accuracy, over all conformations compared to the MR potential. However, significant differences were observed for vibrational relaxation of the $v = 1, j = 0$ state of the H_2 molecule in collisions with He computed using the two surfaces. The limiting value of the quenching rate coefficient on the BMP surface was found to be about three orders of magnitude larger than that of the MR surface. The difference was attributed to the more anisotropic nature of the BMP surface leading to larger values of the off-diagonal elements responsible for driving vibrational transitions. Indeed, it was found that the vibrational quenching of the $v = 1, j = 0$ level was dominated by the transition to the $v' = 0, j' = 8$ level which is driven by the high-order anisotropic terms of the interaction potential.

To explore the behavior of inelastic collisions involving polar molecules at ultracold temperatures, Balakrishnan, Forrey and Dalgarno [23] investigated vibrational and ro-