

FIG. 5: Rate coefficients for the quenching of $\text{CO}(v=1, j=0, 1)$ by collisions with ^4He as functions of the temperature. Reproduced with permission from Balakrishnan et al. [23].

in the $v=0$ and $v=1$ vibrational levels. Fig. 6 shows the Feshbach resonance in the elastic scattering cross sections in the $v=1, j=0$ channel in the vicinity of the $v=1, j=1$ level. The presence of the Feshbach resonance close to the opening of the $j=1$ level has a dramatic effect on the vibrational quenching cross sections from the $v=1, j=1$ level of the CO molecule. Since the Feshbach resonance occurs so close to the threshold of the $v=1, j=1$ channel, its effect on scattering in the $v=1, j=1$ level is similar to that of the zero-energy resonance discussed previously for the $\text{Ar} + \text{D}_2$ system. This is illustrated in Fig. 5 (see also Table I) where we compare the rate coefficients for vibrational relaxation from the $v=1, j=0$ and $v=1, j=1$ levels of the CO molecule. The zero-temperature limiting value of the quenching rate coefficient of the $v=1, j=1$ level is about two orders of magnitude larger than for the $v=1, j=0$ level. Similar Feshbach resonances have also been shown to occur in the vibrational and rotational predissociation of $\text{He}-\text{H}_2$ van der Waals complexes [20]. Forrey et al. [20] has successfully used the effective range theory to predict the predissociation lifetimes of these resonances.

The Feshbach resonances can be used as a very sensitive probe for the interaction potential and also to selectively break or make bonds in chemical reactions. The coupling between the bound and unbound states can be modified by applying an external electric or magnetic field and this provides an important mechanism for creating or eliminating Feshbach resonances and thereby controlling the collisional outcome. Krems have shown that weakly bound van der Waals complexes can be dissociated by tuning a Feshbach resonance using an external magnetic field [52]. In this case the dissociation occurs through coupling between Zeeman levels of the bound

and unbound channels and the magnitude of the coupling is varied by changing the external magnetic field.

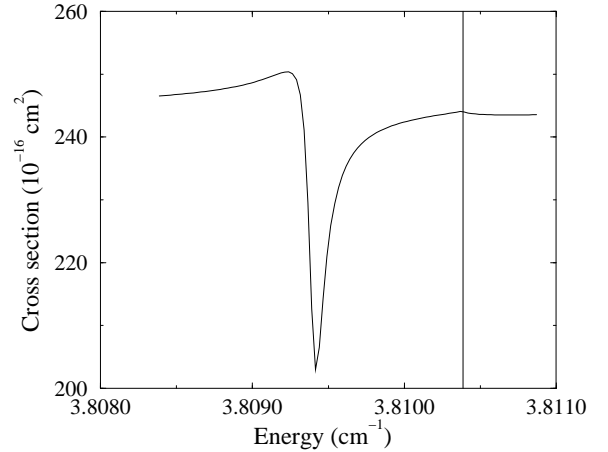


FIG. 6: Feshbach resonance in the elastic scattering cross section of $\text{CO}(v=1, j=0)$ by ^4He atoms. The resonance occurs just below the opening of the $v=1, j=1$ level shown by the vertical line. The energy is relative to the $v=1, j=0$ level of the CO molecule. Reproduced with permission from Balakrishnan et al. [23].

B. Quasi-resonant transitions

While the properties of cold and ultracold collisions are quite different from scattering at thermal energies and quantum effects dominate at low temperatures, a remarkable correlation between classical and quantum dynamics has been discovered in the relaxation of rotationally excited diatomic molecules. Experiments performed nearly two decades ago [53, 54] showed that collisions of rotationally excited diatomic molecules with atoms may result in very efficient internal energy transfer between specific rotational and vibrational degrees of freedom. The energy transfer becomes highly efficient when the collision time is longer than the rotational period of the molecule. This effect has since been termed “quasi-resonant rotation-vibration energy transfer”. The experimental results revealed that the quasi-resonant (QR) transitions satisfy the propensity rule $\Delta j = -4\Delta v$ or $\Delta j = -2\Delta v$ where $\Delta v = v_f - v_i$ and $\Delta j = j_f - j_i$ [53, 54]. This inelastic channel dominates over all other ro-vibrational transitions. The QR transfer is generally insensitive to details of the interaction potential. Rather, the QR process involves conservation of the action, $I = n_v v + n_j j$, where n_v and n_j are small integers. Forrey et al. [21] found that the QR transitions also occur in cold and ultracold collisions of rotationally excited diatomic molecules with atoms and that the process is largely insensitive to the details of the interaction potential even in the ultracold regime. The $\Delta j = -2\Delta v$ QR transition in $\text{He} + \text{H}_2$ collisions [55] is illustrated in Fig. 7