

should be the more stable stereoisomer. Isomer **15** can yield only the observed *cis*-diammine product. If the trigonal-bipyramidal form **15** is a long-lived intermediate, there is, of course, the possibility of polytopal rearrangement to give the other isomers **16** and **17**. We suggest that the energy level difference between isomers **15** and **16** is sufficiently large that this is not an important phenomenon.

It is noteworthy that isomer **17** should be the favored species of the three possible forms. However, this isomer cannot be formed directly on the addition of ammonia, and in order for it to be generated by a polytopal rearrangement it would be necessary to traverse the presumed high-energy state represented by isomer **16**.

The above is only a rationale, alternative to the kinetic "trans effect," applicable to square-planar substitution reactions. We plan to subject this approach to a more rigorous evaluation, primarily through examination of barriers in model five-coordinate complexes relevant to chemistry of this character.

### Seven-Atom and Higher Families

Stereochemical rigidity should be minimal in the seven-atom family. All theoretical or semiempirical attempts to analyze structural facets of seven coordination suggest an undistinguished potential-energy surface. The degree of nuclear displacement required for interconversion of these polytopal isomers is small. A possible distortion mode for the interconversion of the  $D_{5h}$  pentagonal bipyramid and  $C_{2v}$  bicapped trigonal prism is illustrated in Figure 7. All seven-coordinate complexes investigated by nmr techniques have shown ligand atom equivalence, e.g.,  $IF_7$  and  $ReF_7$ .<sup>61</sup> More recently we have been examining a group of seven-coordinate osmium hydrides at very low temperatures in an attempt to discern the transitional region associated with a polytopal rearrangement. The proton nmr spectrum of  $H_2Os[C_6H_5P(OC_2H_5)_2]_3$  is a simple quartet at room temperature, and this quar-

(61) E. L. Muetterties and K. J. Packer, *J. Amer. Chem. Soc.*, **86**, 293 (1964).

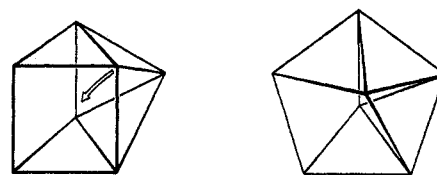


Figure 7. A possible deformation mode for the interconversion of two idealized seven-coordinate polytopal forms. The figure on the left undergoing deformation is the monocapped trigonal prism of  $C_{2v}$  idealized symmetry and the one on the right is the pentagonal bipyramid of  $D_{5h}$  symmetry.

ter begins to broaden at lower temperatures until a single and broad peak obtains at temperatures of about  $-100^\circ$ . We believe that the broadening is due to an intermediate rate of polytopal rearrangement but cannot prove this point until the barrier is elevated through a ligand substitution that introduces significant electronic or steric constraints.

Nmr study of polytopal rearrangements in the seven-coordinate and higher complexes will be difficult at best because rearrangement barriers will be intrinsically very low, the number of discrete complexes of adequate stability is small, and typically the central nuclei have large quadrupole moments. To date, our attempts and attempts by others<sup>62</sup> to detect (nmr) intramolecular rearrangements at low temperatures in species like  $ReH_9^{2-}$ ,  $ReH_8PR_3^-$ ,  $ReH_7(PRe_3)_2$ , and  $Mo(CN)_8^{4-}$  ( $^{13}C$ ) have been unsuccessful. In contrast, rearrangements in the polyhedral borane class of the 7- through 12-atom families have relatively high barriers (20–80 kcal). Rearrangement mechanisms are reasonably well established in some<sup>63</sup> boranes, e.g.,  $B_{10}H_{10}^{2-}$  and its derivatives,<sup>64</sup> and others are under current study in our laboratories and others.<sup>65</sup> Mechanisms established for the polyhedral borane class should serve as realistic, idealized models for polytopal rearrangements in the analogous coordination compound class.<sup>9</sup>

(62) A. P. Ginsberg, *Inorg. Chem.*, **3**, 567 (1964).

(63) For a general review of this subject see ref 6, 9, and 10.

(64) W. R. Hertler, W. H. Knoth, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **86**, 5434 (1964).

(65) For a recent report on the 12-atom carboranes, see H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *ibid.*, **89**, 4218 (1967).

## Quasi-Bound States in Molecular Collisions

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Quasi-bound states are bound species that can spontaneously dissociate, with conversion of part of their energy into the translational energy of unbounded relative motion of the dissociation fragments.

Such a broad definition encompasses a large range of phenomena,<sup>2</sup> depending on the mode of formation and

the nature of the decay products; for example, radioactivity, autoionization, spontaneous emission, predissociation, unimolecular breakdown, etc. In particular,

(2) For a unified quantum mechanical approach to such phenomena see, for example, (a) R. D. Levine, "Quantum Mechanics of Molecular Rate Processes," Oxford University Press, Oxford, England, 1969. See also H. Feshbach, *Ann. Phys. (New York)*, **5**, 537 (1958); **19**, 287 (1962). For an early formulation see (b) O. K. Rice, *Phys. Rev.*, **33**, 748 (1929); **34**, 1459 (1929); **35**, 1551 (1930).

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a quasi-bound molecular aggregate can participate as an intermediate stage in a gas-phase molecular encounter.<sup>3</sup> Here, during the collision, the colliding molecules are temporarily bound together by their attractive interaction.

The participation of such quasi-bound states is manifested experimentally in an increased probability for the colliding molecules to engage in some detectable physical or chemical event. Thus, such pairs enhance the probability of a three-body collision and hence provide an efficient intermediate in third-body-assisted recombination.<sup>3,4</sup> The formation of such pairs may also lead to the appearance of new optical transitions<sup>5,6</sup> absent at low pressures or to deviations from ideal gas behavior<sup>7</sup> due to the reduction in the effective number of molecules. Various relaxation phenomena are also more probable due to the longer interaction time. Examples include enhanced energy transfer<sup>8a</sup> or spin relaxation<sup>8b</sup> in the gas phase.

In general, the energy distribution in the quasi-bound pair, immediately following its formation, reflects the initial state of the colliding molecules. In complex systems (high density of states), internal relaxation (internal conversion) to states of the same total energy but with different internal distribution of energy is expected to result in an equilibrium distribution of energy. The energy distribution in the dissociation products and the distribution of their relative energy should reflect this (possibly partial) equilibration.<sup>9,10</sup>

The most direct experimental evidence for the participation of quasi-bound states in isolated, binary molecular collisions is provided by crossed molecular beams studies.<sup>10,11</sup> It is convenient to contrast these manifestations of their participation with the expected behavior in their absence, *i.e.*, in so-called "direct" collision. For a direct collision the time,  $\tau$ , spent by the

molecules in the interaction region is expected to be of the order of the passage time  $a/v$ , where  $a$  is the range of the interaction region and  $v$  is the velocity. Clearly, there is a justification in referring to the formation and subsequent decay of a quasi-bound (qb) state (a "compound" collision) only if  $\tau$  exceeds  $a/v$ .

An interesting aspect of the longer collision time is the expected angular distribution of the fragments after the collision. Consider a collision of two atoms (in a  $\Sigma$  electronic state), in a plane whose direction is that of the (conserved) angular momentum. Intuitively one expects that when the lifetime of a possible quasi-bound state exceeds the rotational period of the pair, the angular distribution of the atoms after the collision will not show any preferred direction in the plane. The angular distribution into the solid angle  $d\omega$ ,  $d\sigma/d\omega$  ( $d\omega = 2\pi \sin \theta d\theta$ ), is thus expected<sup>12</sup> to behave as  $(\sin \theta)^{-1}$ . In contrast, for direct, hard-sphere collisions,  $d\sigma/d\omega$  is isotropic<sup>12</sup> (*i.e.*,  $d\sigma/d\omega$  is constant). An example is shown in Figure 1. For molecular collisions one should take into account the internal angular momentum of each molecule (and also any electronic component if present), but the expected reflection symmetry of the angular distribution about  $\theta = 90^\circ$  still applies.<sup>13</sup> Similarly, one expects the distribution of energy in the final products to be characteristic of a system in equilibrium. These expectations are not in accord with the early experimental results in crossed molecular beams studies,<sup>14</sup> which were performed for essentially direct collisions. The angular distributions were found to be asymmetric in  $\theta$  and the energy distribution gave no indication of extensive internal relaxation. Subsequent experiments (say Cs + RbBr<sup>10</sup> or K + SO<sub>2</sub><sup>11</sup>) led to results which were more in accord with the above expectations.

Another manifestation of the longer collision time due to qb states is the possible increase in the cross section around the energies of their formation.<sup>15</sup> It is this feature (most notable in nuclear physics) that provides the designation "resonance" for a qb state. It should be emphasized that not every hump in the cross section as a function of the energy is a resonance. No un-

(3) R. D. Levine, *J. Chem. Phys.*, **46**, 331 (1967).

(4) R. E. Roberts, B. B. Bernstein, and C. F. Curtiss, *ibid.*, **50**, 5163 (1969).

(5) A. Watanabe and H. L. Welsh, *Phys. Rev. Lett.*, **13**, 810 (1964); R. G. Gordon and J. K. Cashion, *J. Chem. Phys.*, **44**, 1190 (1966).

(6) (a) R. P. Blickensderfer and G. E. Ewing, *ibid.*, **47**, 331 (1967). (b) Similar results hold for (NO)<sub>2</sub>. For the relevant (electronic) interaction, see E. E. Nikitin, *Opt. Spectrosc. (USSR)*, **9**, 8 (1960).

(7) D. E. Stogryn and J. O. Hirschfelder, *J. Chem. Phys.*, **31**, 1531 (1959); F. T. Smith, *ibid.*, **38**, 1304 (1963); E. A. Guggenheim, *Mol. Phys.*, **11**, 403 (1966).

(8) (a) J. Billingsley and A. B. Callear, *Nature*, **221**, 1136 (1969); (b) R. Bersohn, *Comment. Atom. Mol. Phys.*, **1**, 84 (1969).

(9) In quasi-equilibrium theories (*i.e.*, R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952)) this equilibration is assumed to be complete. See, for example, E. L. Spatz, W. A. Seitz, and J. L. Franklin, *ibid.*, **51**, 5142 (1969). This equilibrium is expected only for complex systems where the density of states is high. Here the initially formed quasi-bound state is the one that can be formed directly from the colliding molecules. Subsequently, more complex internal redistribution of energy can take place, leading to equilibration. Similar effects (internal conversion) are found in the optical spectra of complex molecules where the first state is the one with an allowed dipole transition from the ground state.

(10) (a) W. M. Miller, S. A. Safran, and D. R. Herschbach, *Discuss. Faraday Soc.*, **44**, 108 (1967); for the distribution of translational energies see also (b) L. Matus, I. Opauszky, D. Hyatt, A. J. Mason, K. Birkinshaw, and M. J. Henchman, *ibid.*, **44**, 146 (1967); (c) A. Ding, A. Henglein, D. Hyatt, and K. Laemann, *Z. Naturforsch.*, **A**, **23**, 779, 2090 (1968).

(11) (a) D. O. Ham and J. L. Kinsey, *J. Chem. Phys.*, **48**, 939 (1968); (b) R. Wolfgang, *Accounts Chem. Res.*, **3**, 48 (1970), and references therein.

(12) Let  $b$  be the impact parameter (*i.e.*, the distance of closest approach in the absence of interaction). The angular distribution is, in the classical theory,  $(d\sigma/d\omega) = 2\pi b(db/d\omega) = (b/\sin \theta)/|d\theta/db|$ . For a complex with a given value of the impact parameter and in the absence of correlation between  $b$  and  $\theta$  (*i.e.*, after more than one rotational period of the pair),  $d\sigma/d\omega \sim (\sin \theta)^{-1}$ . See also D. R. Herschbach, *Discuss. Faraday Soc.*, **33**, 149 (1962). For hard spheres one can easily (exercise) evaluate  $b(\theta)$  and find  $(d\sigma/d\omega)$  to be independent of  $\theta$ . Note that these classical arguments do not apply to small angles  $\theta$  (these small deflections correspond to collisions with high values of  $b$ ).

(13) When a system is internally relaxed its evolution is constrained only by the conservation of good quantum numbers. Thus, in a collision with a given total energy those qb pairs that reach equilibrium can be considered to be drawn from a microcanonical ensemble. Conservation of parity thus implies the reflection symmetry about  $\theta = 90^\circ$ . Note that (a) only angular momentum relaxation is required for approximate validity of the argument and (b) no qb states are expected in collisions with high  $b$  (see below). When high  $b$  values can contribute (*i.e.*, in elastic scattering), deviations are expected at small deflections  $\theta$ .

(14) See, for example, D. R. Herschbach in "Molecular Beams," J. Ross, Ed., Interscience, New York, N. Y., 1966.

(15) This reflects the increased probability for the molecules to be in the region of the interaction.

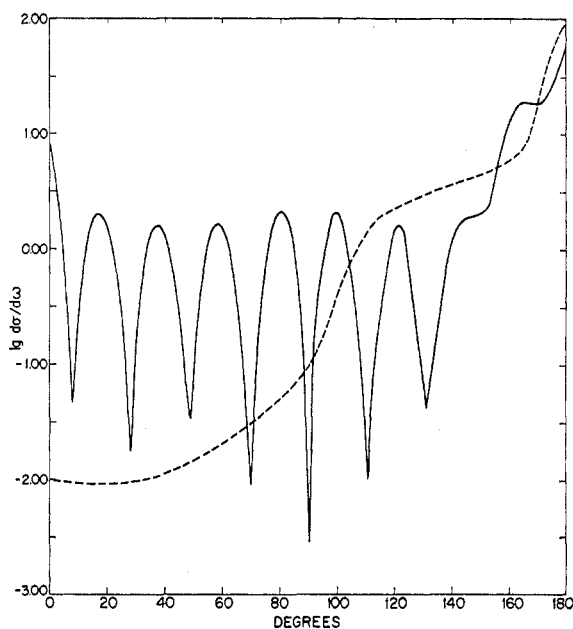


Figure 1. Computed angular distributions for an inelastic collision for compound (full line) and direct (broken line) collisions. The direct angular distribution is essentially backward and hence corresponds to low-impact-parameter (*i.e.*, nearly "head-on") collisions. The compound collision is due to an orbiting state. Thus, very-low-impact-parameter collisions would still proceed *via* a direct mechanism, and these direct contributions enhance the angular distribution at very large deflections. The actual angular distribution for the predominantly compound collision deviates therefore from an exact symmetry about  $\theta = 90^\circ$ .

equivocal direct experimental observation of resonances in cross sections, obtained in crossed molecular beams studies, has been reported to date. The (glory) maxima observed in the (comparatively poor energy resolution) cross sections are *not* resonances as they do not correspond to an increased lifetime or density of states.<sup>2a</sup> Computational results for realistic potentials have definitely indicated the possibility of observing such resonances under improved energy resolution, and evidence is also available from the frequency dependence of the pressure-induced infrared spectra<sup>5</sup> and from the absorption line profile of predissociating (*i.e.*, quasi-bound) states. All these effects have been observed in electron-molecule collisions<sup>16</sup> where similar binding interactions apply.

In a qualitative discussion of quasibound states it is convenient to consider specifically two types (even though it turns out that the distinction is not sharp). The distinction is based on the mechanism of the temporary binding.

**Internal Excitation States.** Here the initial (positive) kinetic energy of relative motion is converted into internal excitation of the colliding molecules. The (attractive) mutual interaction between the excited molecules can then lead to a temporary formation of a bound state. Eventually, before the binary encounter is over, the internal excitation is reconverted into relative translational energy and the molecules separate.

These "internal excitation" quasi-bound states are formed as a result of an attractive interaction between the excited molecules. One expects the energies of such quasi-bound states to correspond to the bound state ("vibrational") energies of the attractive interaction that supports them (*cf.* Figure 2) and, hence, the manifestation of such states should be most pronounced in the energy regimes below the threshold energies corresponding to the different excitation paths. A quantitative discussion of these points is given below.

The first characterization of the internal excitation states is the physical nature of the attractive interaction that supports the bound states. In the simplest situation, involving nonpolar molecules, the potential well is the balance between the long-range (London-type) attractive polarization force and the invariable short-range repulsion. In this case one refers to "van der Waals" quasi-bound states.<sup>17</sup> Other types are clearly possible, including dipolar interactions between polar molecules, and at shorter ranges where electronic overlap occurs, deeper "chemical wells" are also feasible for non-closed-shell systems. The second aspect is the nature of the internal excitation that accepts (removes) the translational kinetic energy of the relative motion. For closed-shell systems, these can be classified in increasing order of energy as rotational, vibrational, and electronic excitation; otherwise (*e.g.*, in<sup>7b</sup> NO + NO) low-lying electronic excited states are often possible, and, for atomic collisions, provide the only available mechanism for internal excitation. Finally, for a given type of interaction and mode of excitation, the possible quasi-bound states can be enumerated using the vibrational quantum numbers of the supporting potential well.

The discussion above corresponds to a weak coupling situation where we have considered the internal excitations during the collision in terms of excitations of the noninteracting collision partners. This point of departure is natural when one is dealing with collisions of simple systems. An alternative point of view centers attention directly on the quasi-bound species. In this "activated state" type enumeration one does not necessarily try to correlate the internal excitations (which store the excess energy) with degrees of freedom of the fragments. This point of view is particularly useful when many quasi-bound states are possible and reduces in the limit to the transition-state method of state counting.<sup>18</sup>

**Orbiting States.** Another manifestation of the attractive molecular interaction are the "orbiting" states which can be formed during noncollinear collisions. Here the effective potential for the radial relative motion is the sum of the attractive interaction  $V(R)$  and the repulsive, long-range, centrifugal potential. For

(17) (a) R. D. Levine, B. R. Johnson, J. T. Muckerman, and R. B. Bernstein, *J. Chem. Phys.*, **49**, 56 (1968); (b) W. Erlewein, M. von Seggern, and J. P. Toennies, *Z. Phys.*, **211**, 35 (1968); M. von Seggern and J. P. Toennies, *ibid.*, **218**, 341 (1969); (c) P. G. Burke, D. Scrutton, J. H. Tait, and A. J. Taylor, *Proc. Phys. Soc., London (At. Mol. Phys.)*, **2**, 1155 (1969).

(18) F. H. Mies, *J. Chem. Phys.*, **51**, 798 (1969).

(16) J. N. Bardsley and F. Mandl, *Rep. Progr. Phys.*, **21**, Part 2, 471 (1968).

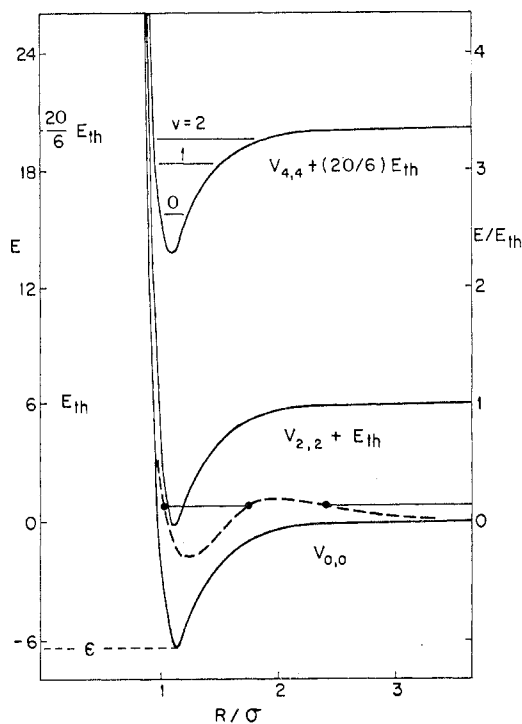


Figure 2. Interaction potentials between an atom and a homonuclear rigid rotor in the  $j = 0, 2$ , and  $4$  rotational states, in units of the lowest threshold energy ( $E_{th} = j(j+1)B_e, j = 2$ ). Shown also (in dashed lines) is the effective potential for a collision with  $j = 0$  and a finite angular momentum of relative motion ( $l = 12$ ). The three classical turning points for the indicated energy are marked as dots. The positions and vibrational quantum numbers of the bound states of the upper potential are indicated. These will appear as quasi-bound states for collisions in an energy interval below the second threshold (cf. Figure 5).

sufficiently small values of the angular momentum<sup>19</sup> the effective potential will have both a minimum and a maximum (cf. Figure 2). Classically, when the total energy is below the potential maximum, the minimum region is inaccessible. During such a collision the two systems cannot approach nearer than their outermost turning point. Quantum mechanically there is a nonzero probability for the system to penetrate the barrier and reach the inner region. At most energies (below the barrier) this probability is negligibly small. Exceptions occur at such energies that correspond to the bound state energies that would obtain had we modified the potential beyond the maximum point so that it had only two (internal) turning points.<sup>20</sup> Semiclassically one can say that at such energies there is constructive interference between the waves scattered at the two

(19) For a Lennard-Jones 12-6 potential, the effective radial interaction is  $4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6] + \hbar^2 l(l+1)/2\mu R^2$ . This potential has both a minimum and a maximum when  $0 < [\hbar^2 l(l+1)/2\mu\epsilon\sigma^2]^{1/2} < 6(5^{-1/6})$  and the height of the maximum is always below  $0.8\epsilon$ .  $b$  is related to  $l$  by  $l \approx (2\mu E/\hbar^2)^{1/2} b$  (here  $\mu$  is the reduced mass). Low  $l$  values are sometimes referred to as  $s, p, d, \dots$  (partial) waves.

(20) The precise way of doing this does not change the results significantly. Similar remarks apply also to the general case where the molecular interaction itself may have a hump of the required shape (leading to so-called "shape" or "potential" resonances). This may happen<sup>21</sup> for adiabatic potentials in the case of curve crossing at large separations or along the reaction coordinate on a potential energy surface.<sup>22</sup>

(21) R. D. Levine, B. R. Johnson, and R. B. Bernstein, *J. Chem. Phys.*, **50**, 1694 (1969).

inner turning points (i.e., there is an integral number of wavelengths between these points), and hence tunneling into the internal region is enhanced. The formation of orbiting states is thus restricted to low energies,<sup>19</sup> below the barrier height. One also expects similar effects when the potential energy surface for a reactive collision has a well along the reaction coordinate.<sup>22</sup>

For large values of the angular momentum, the effective potential is purely repulsive and cannot support any bound (or quasi-bound) states. Thus, neither internal excitation nor orbiting states are expected to participate in collisions with high impact parameters.

### Theory of Compound Collisions

The quantitative analysis of the role of quasi-bound states during a collision can be discussed using the state expansion method<sup>2</sup> for the total wave function describing the collision. Consider, for simplicity, the collision of a structureless atom with a diatomic molecule.<sup>17</sup> The Hamiltonian  $h$  describing the collision partners is the internal Hamiltonian of the diatomic molecule and has a sequence of eigenvalues  $E_n$  and (orthonormal) eigenfunctions  $\phi_n(r)$  describing the ground and excited states of the diatomic molecule. Here  $r$  is the set of internal (rotational and vibrational) coordinates of the diatomic. The total Hamiltonian  $H$  describing the collision can be written as<sup>23</sup> in eq 1, where

$$H = h(r) + K + V(R, r) \quad (1)$$

$K$  is the operator for the kinetic energy of the relative motion and  $V(R, r)$  is the mutual interaction. The Schrodinger equation to be solved for  $\psi$  is eq 2,

$$(E - H)\psi(R, r) = 0 \quad (2)$$

subject to the boundary conditions that before the collision the diatomic was in a specified internal state. Here  $E$  is the known total energy (the sum of the initial internal and kinetic energies).

One can eliminate the explicit dependence on the internal coordinates ( $r$ ) in eq 2 by the state expansion 3.

$$\psi = \sum_n F_n(R) \phi_n(r) \quad (3)$$

Introducing (3) into (2), multiplying from the left by  $\phi_m^*(r)$ , and integrating over  $r$  using the orthogonality of the eigenfunctions of  $h$ , one obtains eq 4. Here

$$[E - E_m - K - V_{m,m}(R)]F_m(R) = \sum_{n \neq m} V_{m,n}(R)F_n(R) \quad (4)$$

$V_{m,n}(R) = \langle \phi_m | V(R, r) | \phi_n \rangle$  and the Dirac brackets

(22) (a) J. O. Hirschfelder, H. Eyring, and B. Topley, *ibid.*, **4**, 170 (1936). (b) M. S. Child, *Mol. Phys.*, **12**, 401 (1967). Note that this is to be expected, since, in terms of a reaction coordinate  $s$ , the reaction is described in terms of a one-dimensional motion along  $s$ . Thus one can also expect that internal excitation quasi-bound states will participate in reactive collisions, the internal excitation leading to a bounded motion along  $s$ .

(23) Our simple model corresponds to an electronically adiabatic collision between a closed shell atom and a homonuclear diatomic molecule, and  $V$  is the "potential energy surface."  $R$  is the relative separation, and the total center of mass is at rest.

denote integration over  $r$  only. Each term in (3) is referred to as a channel, and  $V_{n,n}(R)$  is the interaction in the channel  $n$  where the internal state is  $\phi_n$ . One can obtain a similar set of equations for reactive collisions by considering the motion along the reaction coordinate.<sup>2</sup> Each term in (3) provides only an approximate description of the collision since the perturbation  $V$  can induce transitions between the different internal states. If initially the molecule was in the  $m$ th state, the zeroth approximation retains only the  $m$ th term, thus allowing elastic collisions only and neglecting any possibility of excitation.

Computational methods aimed at the exact numerical solution of sets of coupled eq 4 with the appropriate boundary conditions have been the subject of much recent discussion.<sup>24</sup> One knows<sup>25</sup> that the accuracy of the solution improves with increasing number of terms in (in practice, finite) expansion 3, and convergence has been demonstrated in simple cases (cf. Figure 3). Most of the detailed computations refer to models of rotational excitation where the diatomic is taken to be a rigid rotor, but neither the general theory nor the computational methods are restricted to this case.

**Computational Results.** Figures 2–5 show typical input and output of such computations. Figure 2 shows the molecular interactions used. Shown are the different attractive "channel potentials"  $V_{n,n}(R)$ . These have been shifted so that their asymptotic values correspond to the rotational excitation energies of the diatomic. In the simplest situation (subexcitation collisions) the molecule is initially in the ground rotational state and the total energy is below the threshold for excitation.<sup>26</sup> For s-wave collisions, quasi-bound states can be formed when the diatomic is internally excited during the collision.

For such elastic collisions the computational results are conveniently summarized in terms of a phase shift  $\delta$  (Figure 3). Over most of the subexcitation energy interval the phase is a rapidly decreasing function, as is expected for direct, rapid collisions, where  $(d\delta/dk) \simeq -R_{tp}$ .  $R_{tp}$  is the classical turning point and  $k$  is the wave vector ( $E = \hbar^2 k^2 / 2\mu$ ). The typically resonance behavior is seen in the rapid increase of  $\delta$  by  $\pi$ . Since the elastic cross section receives a contribution proportional to  $\sin^2 \delta$  the resonance behavior will be reflected by the cross section.<sup>27</sup> The resonances have been enumerated by the vibrational quantum numbers of the supporting interaction. As is discussed below, the

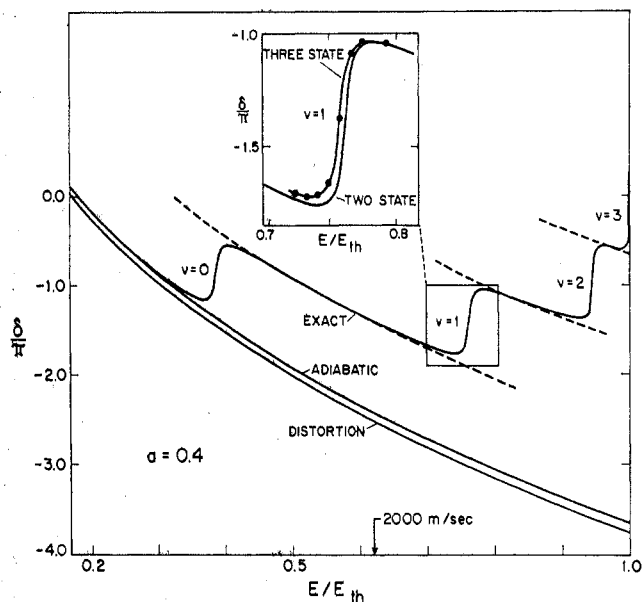


Figure 3. Phase shift for s-wave subexcitation collisions in an atom-homonuclear rigid rotor collision. The resonances (increase of  $\delta$  by  $\pi$ ) are identified by the vibrational quantum number of the bound states of the supporting interaction (*i.e.*, the interaction between the rotationally excited molecule and the atom). The insert demonstrates the convergence of the calculation. Increasing the number of terms in expansion 3 should monotonically increase the phase. Retaining the states  $j = 0, 2, 4$  is seen to ensure convergence, as the addition of  $j = 6$  (dots) does not alter the results significantly. Shown also are the direct phase shifts obtained in the distortion and adiabatic decoupling approximations. The dashed lines represent the adiabatic phase shifted by multiples of  $\pi$ . Since  $\delta$  is only meaningful modulo  $\pi$ , the direct adiabatic phase accurately reproduces the exact phase, away from the resonances (results from ref 17a).

resonance positions can be approximated by the vibrational energies. Figure 4 compares the exactly computed resonance positions with such calculated values for different magnitudes of the asymmetry of the interaction potential.

At higher energies the excitation of the  $j = 2$  rotational state is possible. Figure 5 shows the transition probability for the  $j = 0 \rightarrow 2$  transition as a function of  $E$ . As is clear from Figure 2, for  $(E/E_{th}) < 2.5$  the collision is expected to be direct. However, below the threshold for the excitation of the  $j = 4$  state internal excitation resonances are possible. The form of the transition probability is not Lorentzian since direct processes are possible.<sup>28</sup>

### Decoupling Approximation

The qualitative and semiquantitative interpretation of the role of quasi-bound states is conveniently carried out using the decoupling approximation.<sup>25</sup> Here the interaction responsible for the formation and decay of the qb states is "turned off," thus approximating the qb states as ordinary vibrational bound states whose energy can be computed using known procedures. The reintroduction of the coupling interaction to first order enables us to compute (approximate) decay rates

(24) (a) B. R. Johnson and D. Secrest, *J. Chem. Phys.*, **48**, 4682 (1968); (b) D. J. Diestler and V. McKoy, *ibid.*, **48**, 2941 (1968); (c) R. G. Gordon, *ibid.*, **51**, 14 (1969).

(25) R. D. Levine, *ibid.*, **49**, 51 (1968).

(26) The excitation occurs due to the lack of spherical symmetry of the potential  $V(R,r)$  between the atom and the diatomic. For a homonuclear diatomic the change in the internal angular momentum must be even.

(27) Note however that: (a) the decreasing phase shift can also lead to peaks in  $\sin^2 \delta$  whenever  $\delta$  decreases through  $\pi/2$ , *i.e.*, not every peak is a resonance; (b) in the resonance region  $\sin^2 \delta$  will be peaked at the resonance energy (the inflection of  $\delta$ ) only if the background direct phase is zero at that energy. The shape of  $\sin^2 \delta$  is therefore not necessarily Lorentzian. See also Figure 5 and U. Fano, *Phys. Rev.*, **124**, 1866 (1961).

(28) (a) R. D. Levine, M. Shapiro, and B. R. Johnson, *J. Chem. Phys.*, **52**, 1755 (1970); (b) J. T. Muckerman, *ibid.*, **50**, 627 (1969).

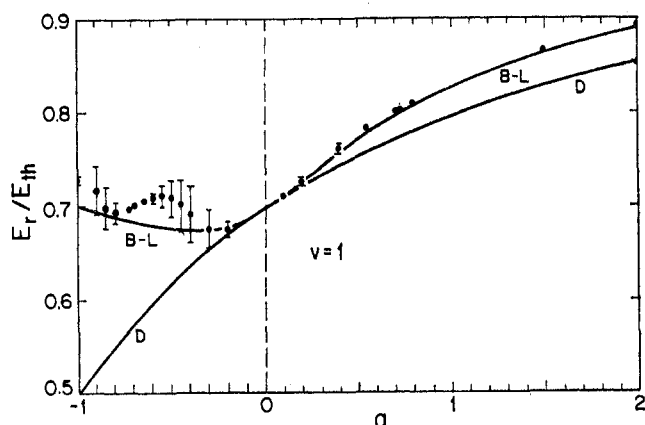


Figure 4. A composite plot showing the exactly computed resonance positions (dots) and decay rates (bars) vs. the assumed magnitude of the asymmetry of the potential,  $\alpha$ . The results of the decoupling approximation for the resonance positions are indicated as D (distortion approximation) and B-L (approximate adiabatic approximation) (results from ref 17a).

of quasi-bound states (and also transition probabilities) by a simple quadrature.<sup>28</sup>

**Subexcitation Collisions.** Consider for simplicity the case when only one ground (say  $m$ ) and one excited state ( $n$ ) is retained in expansion 3.

After decoupling (*i.e.*, on neglecting the coupling  $V_{n,m}$ ) we obtain (the distortion approximation)

$$(E - E_m - K - V_{m,m})F_m^\circ(R) = 0 \quad (5)$$

and

$$(E - E_n - K - V_{n,n})F_n^\circ(R) = 0 \quad (6)$$

Since  $E > E_m$  (and  $V_{m,m} \rightarrow 0$  as  $R \rightarrow \infty$ ), eq 5 will have a solution for any  $E$  and can be solved efficiently using simple procedures. In eq 5 the molecule is constrained to be in the internal state  $m$  during the encounter so that no internal excitation can take place. The resulting phase shift  $\delta^\circ$  is the (distortion) decoupling approximation and is a lower bound<sup>25</sup> to the exact phase (*cf.* Figure 3). For non-s-wave collisions  $V_{m,m}$  may still give rise to orbiting states, and these will appear as resonances in  $\delta^\circ$ . The (distortion) decoupling approximation thus neglects those corrections due to the possibility of internal excitation during the collision and retains only the effects of the (distortion) interaction  $V_{m,m}$ .

For subexcitation collisions  $E < E_n$  and hence eq 6 will have solutions only for particular values of  $E$ ; *i.e.*, eq 6 is an eigenvalue equation for the vibrational bound state energies of  $V_{n,n}(R)$ . These eigenvalues are the (distortion) decoupling approximation to the resonance positions<sup>29</sup> (*cf.* Figure 4). It is clear that the results are only satisfactory at low asymmetry (*i.e.*, when  $V_{n,m}$  is small) and that improved procedures are required. Physically, for slow collisions, the molecule may adjust adiabatically under the perturbation. In other words, the internal state during the collision may

(29) Note that the introduction of the coupling will not only lead to a decay of the bound state but also to a shift in the resonance position. This "level shift" is not necessarily of a definite sign.

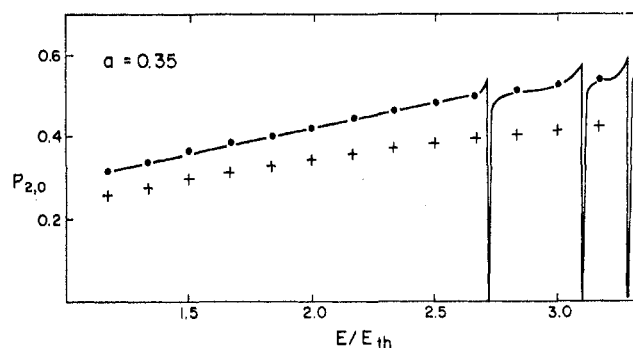


Figure 5. Transition probability for rotational excitation  $j = 0 \rightarrow 2$  of a rigid rotor (in s-wave collisions). The resonances are due to internal excitation of the rotor to the  $j = 4$  state (*cf.* Figure 2). The crosses refer to  $P_{2,0}^\circ$  obtained by retaining only two terms in expansion 3 while the dots refer to retaining two terms in expansion 7 using an adiabatic basis. Thus, the decoupling of the closed channels in an adiabatic basis provides a satisfactory account of the transition probability for direct collisions (results from ref 28).

be modified by a (local) admixture of excited states. To treat these modifications we consider a more general formulation of the decoupling procedure.

**Adiabatic Decoupling.** The resolution (eq 3) into channels is not unique. Equivalent descriptions are easily obtained by a unitary transformation. Thus, let  $\mathbf{C}$  be an orthogonal matrix and define the transformation  $\chi = \mathbf{C}\phi$  and  $\mathbf{G} = \mathbf{C}\mathbf{F}$ ; then eq 7 is an equivalent

$$\begin{aligned} \psi &= \mathbf{F}^T \phi = \mathbf{G}^T \chi \\ &= \sum_n G_n \chi_n \end{aligned} \quad (7)$$

description. In general, the elements of  $\mathbf{C}$  can be functions of  $R$ , and it is convenient to impose the restriction that, as  $R \rightarrow \infty$ ,  $\mathbf{C} \rightarrow \mathbf{I}$ . Hence, at large separations, where individual terms in expansion 7 have physical significance, all equivalent descriptions yield identical results for the individual channels. Since the new basis functions  $\chi_n(r|R)$  are also orthonormal (with respect to integrations over  $r$ ) one can derive a set of coupled equations for the  $G_n$  values (eq 8). Here  $H_{n,m}(R)$

$$[E - H_{m,m}(R)]G_m(R) = \sum_{n \neq m} H_{m,n}(R)G_n(R) \quad (8)$$

$= \langle \chi_n | H | \chi_m \rangle$  and, in contrast to case 4,  $h$  and  $K$  are not necessarily diagonal. A particularly useful choice of  $\mathbf{C}$  is the adiabatic one, defined so that eq 9 obtains,

$$E_{m,m}(R)\delta_{n,m} = \langle \chi_m | h + V | \chi_n \rangle \quad (9)$$

*i.e.*, the adiabatic basis  $\chi$  diagonalizes the interaction terms  $h + V$  at any  $R$ . The coupling terms  $H_{n,m}(R)$  are then due to the nondiagonal elements of the kinetic energy operator. When curve crossing is possible, *i.e.*, when the equation  $E_n + V_{n,n}(R) = E_m + V_{m,m}(R)$  has a solution for a real value of  $R$ , these "non-adiabatic" coupling terms,  $\langle \chi_m | K | \chi_n \rangle$ , can become quite large.<sup>21</sup> Also due to the noncrossing rule, the channel potential  $E_{m,m}(R)$  may have a hump in the crossing region and the classification of the quasi-bound states depends on the particular basis used. In general, however, the (distortion) basis  $\phi$  is more useful

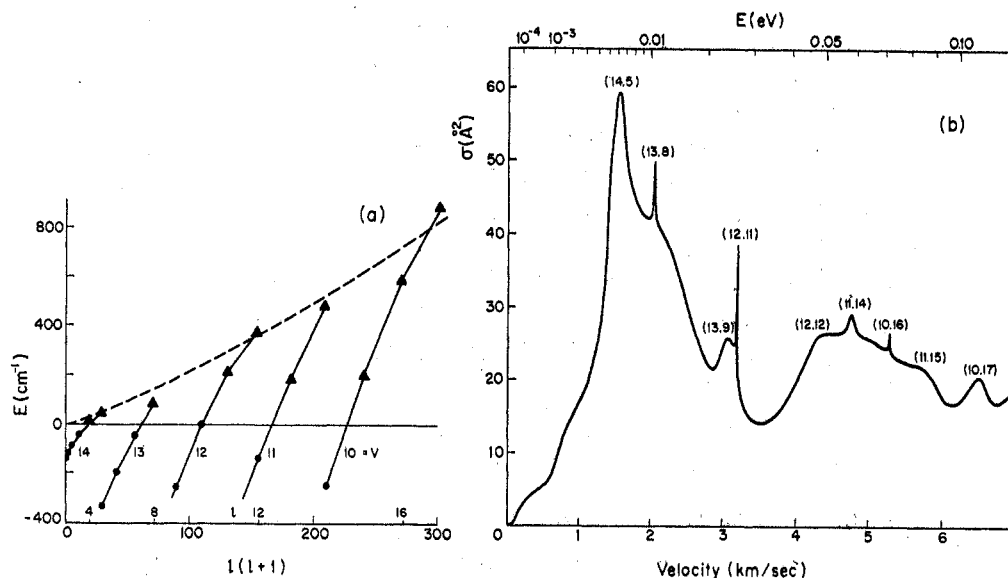


Figure 6. Orbiting resonances in H + H collision under the ground singlet potential. (a) The spectrum of orbiting (triangles) and neighboring bound states (dots) of the singlet potential vs. the orbital angular momentum  $l$ .  $v$  is the vibrational quantum number. The limiting curve for dissociation (LCD) (showing the maximum barrier height at  $l(l+1)$ ), is indicated as a broken line. (b) The computed cross section in the region of the orbiting resonances indicated in (a). The resonances are designated by  $v, l$  quantum numbers of the corresponding quasi-bound states. Thus the  $v, l$  resonance appears in the  $l$ th partial wave (results from (a) T. G. Waech and R. B. Bernstein, *J. Chem. Phys.*, **46**, 4905 (1967); (b) M. E. Gersh and R. B. Bernstein, *Chem. Phys. Lett.*, **4**, 221 (1969).)

for decoupling when  $V_{n,m}$  is weak while the (adiabatic) basis  $\chi$  is more useful at larger  $V_{n,m}$ . The improvement possible using an adiabatic basis is seen in Figures 4 and 5. The phase shift is due to the (adiabatic) channel interaction  $E_{m,m}(R)$  while the bound states are the eigenvalues of  $E_{n,n}(R)$ .<sup>30</sup> Note that the formation and decay of internally excited qb states are thus non-adiabatic processes, being transitions between two adiabatic potentials.

**Complex Systems.** A more elaborate discussion is required for complex systems.<sup>2</sup> Consider subexcitation collisions, with  $m$  as the initial channel. The coupling  $V_{n,m}$  that leads to the formation of quasi-bound states need not be nonzero for all channels  $n$ . Only states in channels  $n$  such that  $V_{n,m} \neq 0$  can be formed directly from the initial channel. However, even though  $V_{n',m}$  may be zero (or very small), if  $V_{n',n} \neq 0$ , states in channel  $n'$  can be excited indirectly by the path  $m \rightarrow n \rightarrow n'$ . This is the phenomenon of internal relaxation that eventually may spread the excitation over the many possible states (of equal total energy) in complex systems and lead to equilibration. Similar mechanisms (internal conversion) operate in the optical spectra of complex systems. Here  $V_{n,m}$  is the optical transition probability from the ground state. The initial (dipole allowed) excitation is to a particular channel(s), which is only one component of the total wave function. The coupling to other channels spreads the excitation.<sup>31</sup> (As in (3) or (7) the resolution into channels (which are not eigenfunctions of  $H$ ) is based

on describing the excited states of the system using an approximate Hamiltonian. As noted earlier, a channel resolution is more useful in weak coupling situations.)

**Orbiting Collisions.** For non-s-wave collisions the channel interaction can also support orbiting states. Figure 6 shows the results obtained for a low-energy collision of two H atoms under the singlet potential. The orbiting resonances are clearly reflected in the energy dependence of the cross section. While these resonances have not yet been resolved in a collision experiment, these quasi-bound states have mostly been identified in the optical spectra of  $\text{H}_2$ . Note that the potential used was not the Heitler-London potential (which would correspond to the distortion decoupling) but the best available adiabatic potential. Here the closed channels are much higher in energy, and no internal excitation states are possible.

Both the orbiting resonances and the rotational subexcitation resonances occur at different energies for different partial waves. For molecular collisions, the cross section receives contributions from many partial waves and hence the effect of a resonance in a single partial wave is small. More distinct effects are expected when a resonance appears at about the same energy in several partial waves. In particular this is expected to be the case for electronic subexcitation collisions (say as in charge-transfer states). For rotational (or vibrational) subexcitation similar bunching could be achieved using heavier diatomics.

**Transition Probabilities.** The simplest description of transitions which decouples the excited states is to retain only those terms in (3) for which  $E > E_n$ . The solution of the appropriate set of coupled equations (eq 4) defines the transition probability  $P_{n,m}^0$  that neglects the role of closed ( $E < E_n$ ) channels. The

(30) Strictly speaking this is an approximate procedure since one should add the matrix elements of  $K$  to the channel potentials.<sup>21</sup>

(31) (a) B. R. Henry and M. Kasha, *Annu. Rev. Phys. Chem.*, **19**, 161 (1968); (b) J. Jortner and M. Bixon, *Israel J. Chem.*, **7**, 189 (1969).

presence of orbiting states will be manifested in  $P_{n,m}^{\circ}$ .<sup>32</sup> Results of such computations are in good agreement with exact results when the coupling to the closed channels is weak and when the closed channels are of high thresholds. Otherwise improved approximations are obtained by truncating expansion 7 rather than expansion 3, *i.e.*, by incorporating the high excited states in an adiabatic fashion. Typical results are shown in Figure 5.

The accurate approximations for the direct transition probabilities still require the solution of a set of coupled equations (albeit of a smaller dimensionality than the original set). Simpler approximations (that do not however conserve probability) are obtained by incorporating the coupling  $V_{n,m}$  that leads to the transition to first order only.<sup>28,33</sup> In particular, by a suitable choice of  $C$  one can often obtain satisfactory results using this approach. These studies have also led to a better understanding of the statistical approximation,<sup>34</sup> It is now clear that statistical methods for the cross section are equally valid for strongly coupled direct collisions and that no physical "complex" or transition state need to be formed. It is only on the level of angular distribution that a distinction between direct and compound collisions is required in a statistical theory.

**Lifetimes.** A convenient characterization of the position and lifetime of a quasi-bound state is in terms of the line shape  $A(E)$ . For a single, isolated, state  $A(E)$  is the weight of the state in the total wave function at an energy  $E$  and can be parametrized in the Breit-Wigner form<sup>2</sup>

$$A(E) = \pi^{-1} \frac{\Gamma/2}{(E - E_r)^2 + (\Gamma/2)^2}$$

Here  $\Gamma$  is the width of the resonance, being the range of energies over which the resonance contributes significantly. As expected on the basis of the uncertainty principle, the lifetime is given by  $\hbar/\Gamma$ .  $E_r$  is referred to as the resonance energy (or position), as it would correspond to the energy of a state having an infinite lifetime.

One expects the lifetime of orbiting states to decrease as their energies increase toward the top of the barrier (where tunneling is faster). Very near the top, lifetimes are expected to be of the order of vibrational periods ( $10^{-13}$  sec), but to increase rapidly as we go further below. Computational results for  $H + H$  orbiting resonances in the singlet potential (Figure 6)

(32) An orbiting resonance in channel  $m$  will increase the probability of the molecules in channel  $m$  to be in the interaction region and hence will tend to enhance the transition probability to channel  $n$  (see ref 17b).

(33) In  $P_{n,m}^{\circ}$  one neglects the coupling to the closed channels but treats  $V_{n,m}$  exactly (*i.e.*, to infinite order).

(34) See, for example, Chapter 3.5 of ref 2a, see also J. C. Light, *Discuss. Faraday Soc.*, **44**, 14 (1967), and R. D. Levine and B. R. Johnson, *Chem. Phys. Lett.*, **4**, 365 (1969).

indicate a range of lifetimes from  $10^{-13}$  to  $10^{22}$  sec. For internal excitation states, the lifetime is expected to increase with increasing strength of the coupling between open and closed channels. For strong coupling this simple relation breaks down (Figure 4), and improved procedures are necessary<sup>25,28</sup> for the approximate computation of decay rates.

For rotational subexcitation collisions, the larger values of  $\Gamma$  correspond to lifetimes of the order of vibrational periods, but much longer lifetimes are possible. In general, for an isolated state, a lifetime shorter than a vibrational period is not very meaningful either experimentally or theoretically.<sup>35</sup> In complex molecules there is the additional effect of internal relaxation, and when the density of states is high, lifetimes can be estimated from quasi-equilibrium considerations.<sup>2</sup>

In concluding we note that: (1) There is both experimental and theoretical evidence for the participation of quasi-bound states in molecular collisions at thermal and somewhat higher energies. (2) Experimentally, their participation implies a longer collision time and a tendency toward internal relaxation, thus leading to a symmetric angular distribution and an equilibration of energy for the products. Resonances in the cross section can also be observed under improved energy resolution. (3) The theoretical studies have developed computational methods that can treat (exactly) both direct and compound collisions. Simultaneously useful approximation methods have been developed. These show that the participation of quasi-bound states depends on the molecular interaction having an attractive part. Even the "weak" van der Waals interaction can support quasi-bound states. These studies have also improved our understanding of the statistical approximation and the transition-state theory. (4) In the future, one could hope for better experimental energy resolutions and the observation of compound collisions phenomena (and their implications) in an increasing number of instances. Theoretically, one should expect a better understanding of the mechanisms of molecular attraction that can support quasi-bound states and improved procedures for the description of the case when there are several (or many) quasi-bound states in a short energy interval.

*I wish to acknowledge the benefit of a very fruitful collaboration with Professor R. B. Bernstein and Drs. B. R. Johnson, J. T. Muckerman, and M. Shapiro.*

(35) We thus require that the relative motion spans at least one vibrational period in the bounded region. Consider Figure 2 where internal excitation (or deexcitation) occurs primarily near the inner classical turning point, where the relative separation starts to increase. One expects therefore that the lifetime be at least the time required for the relative motion to be reflected once by the outer turning point of the upper potential and return to the inner turning point. There the molecule is either deexcited into an open channel or the bounded motion continues, with possible deexcitation following the second, third, ... vibrations.