Transition probabilities from highly excited states of anharmonic oscillators under the effect of three-dimensional collisions

M.L. Strekalov

Institute of Chemical Kinetics and Combustion, Siberian branch of Russian Academy of

Sciences, 630090 Novosibirsk, Russia

Abstract

The closed form solution for Morse oscillator transition probabilities valid for highly excited states has been obtained. As an example, we have considered large Δn transitions in vibrationally inelastic scattering of I_2 molecules from two isotopic targets H_2 and D_2.

1. Introduction

Despite considerable progress in numerical computations, the use of simple models in vibrational relaxation is still effective, since they make it possible to rather easily estimate vibrational transition probabilities with knowledge of the interaction potential. Obviously, the models are also useful in studies of the sensitivity of results to the potential parameter variations. Besides, in such an approach, recommendations can be given concerning the estimates of the intermolecular potential parameters. Numerous attempts to develop analytical approaches for vibrationally inelastic atom-molecule collisions are available in the literature (see, for example, reviews [1-6] and references therein). However, some of the models have serious inherent demerits that make them less reliable and accurate as compared to fully quantum calculations, quasiclassical, semiclassical, and classical trajectory calculations. Many of the models are based on the first-order perturbation theory and therefore cannot be applied for multiquantum processes. Exceptions are the forced harmonic oscillator model [1-4, 7] and the Bessel uniform approximation [8-11] developed for collinear collisions of an atom with a harmonic oscillator.

This Letter deals with the analytical approaches to the problem of a Morse oscillator interacting with a structureless atom in three-dimensional collisions, and incorporates the effects of rotational degrees of freedom in the infinite order sudden (IOS) approximation.

2. The forced highly excited oscillator

Consider an inelastic collision of a diatomic molecule BC in the state $|njm>$ with an atom A that results in the state $|n'j'm'>$ where n is the vibrational quantum number, and j,m are the rotational quantum numbers. The interaction potential is written as usual

$$V(r,R,\gamma) = \sum_{\lambda=0} V_\lambda(r,R) P_\lambda(\cos\gamma) \quad , \tag{1}$$

where R is the distance from the atom A to the center of mass of BC, r the distance between B and C and γ the angle between vectors $\mathbf{r}$ and $\mathbf{R}$. The classical path Hamiltonian is given by

$$H = \frac{p^2}{2M} + V_M(r) + B\mathbf{J}^2 + V(r_e,R,\gamma) - xf(t) \quad , \tag{2}$$

where $V_M(r)$ is the intramolecular potential chosen in the form of Morse oscillator, M the reduced mass of the molecule, $B = \hbar^2/2Mr_e^2$ the rotational constant, $x = r - r_e$ the displacement and $f(t)$ the external force

$$f(t) = -\sum_{\lambda=0} \left(\frac{\partial V_\lambda}{\partial r}\right)_e P_\lambda(\cos\gamma) \tag{3}$$

The above representation corresponds to the intermolecular potential expansion in powers of small vibrational amplitude. The trajectory of the relative motion $R(t)$ is determined by the isotropic part of the potential $V_0(r_e,R)$.

To proceed further, we shall suppose that the molecule actually does not rotate during a collision. The IOS approximation may be used to consider only the rotational degrees of freedom, leaving the vibrational degrees of freedom to be treated in a semiclassical manner. The IOSA is ideally suited for heavy molecules with closely spaced rotational levels colliding with light atoms. Within the IOS approximation the probability of vibrational transition from the state n to the state n' is given by a simple formula [12]

$$P_{nn'} = \frac{1}{2j+1} \sum_{j'm'm} |< njm \,|\, S \,|\, n'j'm' >|^2 = \int_{-1}^{1} |S_{nn'}(\gamma)|^2 \frac{d(\cos\gamma)}{2} \quad , \tag{4}$$

where the S matrix elements depend on the rotational coordinate as on a parameter. Now turn to the exponential approximation for the scattering matrix. Its characteristic feature is that even the first-order Magnus approximation gives the exact solution for a harmonic oscillator under the action of external force [13]

$$S = \exp\left[-i\left(\frac{2M\omega_e}{\hbar} \right)^{1/2} \delta(\gamma) x \right] \,, \tag{5}$$

where $\delta(\gamma)$ is the change in action of the active molecule evaluated along a classical trajectory

$$\delta(\gamma) = \left(\frac{\hbar}{2M\omega_e} \right)^{1/2} \sum_{\lambda=0} P_\lambda(\cos\gamma) \frac{1}{\hbar} \int_{-\infty}^{\infty} \left(\frac{\partial V_\lambda}{\partial r} \right)_e \cos[\omega(\bar{n})t] dt \tag{6}$$

Here ω_e is the equilibrium oscillation frequency, $\omega(\bar{n})$ is some mean transition frequency (see below). We would like to emphasize once again that this result is valid in the first order of Magnus approximation for a Morse oscillator, and is exact for a harmonic oscillator.

In principle, the model of harmonic oscillator does not describe highly excited vibrational states, thus problems involving such states do not have exact analytical solutions in collision theory. For highly excited states we can apply the correspondence principle, and use action-angle variables. With this aim in mind, it is convenient to transform the Cartesian variable x in action-angle coordinates I,α [14]

$$x = \left[\frac{\hbar(2N+1)}{2M\omega_e} \right]^{1/2} \ln\left(\frac{1 + \sqrt{1 - w(\bar{n})^2} \sin\alpha}{w(\bar{n})^2} \right) \tag{7}$$

For convenience of notation, we introduce the quantity

$$w(\bar{n}) = 1 - \frac{2\bar{n}+1}{2N+1} = \frac{\omega(\bar{n})}{\omega_e} \tag{8}$$

According to the correspondence principle, the transition frequency $\omega_{n'n}$ is to be equal to

$(n' - n)\omega(\bar{n})$ where the mean quantum number $\bar{n}$ is related to the classical action variable I

as $I = (\bar{n} + 1/2)\hbar$. For the Morse oscillator $\bar{n}$ is exactly equal to $(n + n')/2$. In the above

equations N is the number of bound states or, in another notation, $(2N + 1)^{-1} = x_e$ where x_e

is the anharmonicity constant [15]. Equations (7), (8) give the case of harmonic oscillator [16] in

the limit $N \to \infty$.

The correspondence principle for strongly coupled states [4] provides an approximate

expression for S-matrix elements between states n and n' of a highly excited bound system

$$S_{nn'} = \frac{1}{2\pi} \int\limits_{-\pi}^{\pi} \exp\left[i\Delta n \alpha - i\delta(\gamma)\sqrt{2N+1} \ln\left(\frac{1 + \sqrt{1 - w(\bar{n})^2} \sin\alpha}{w(\bar{n})^2} \right) \right] d\alpha \ , \quad (9)$$

where $\Delta n = n' - n$. In general, equation (9) is only true in the limit of high $n(n')$ and low Δn,

i.e., the smaller the ratio $\Delta n / n_<$, the larger the range of validity of the strong-coupling

correspondence principle (SCCP) approximation. Now let us evaluate this integral by the

stationary phase method treating the quantity $\delta(\gamma)\sqrt{2N+1}$ as a large parameter. By

approximating the $\ln(...)$ function in Eq. (9) by a quadratic term in $\alpha - \alpha_k$, one obtains the

approximation for $S_{nn'}$ valid for two stationary phase points $\alpha_k = \pm\pi/2$, namely:

$$|S_{nn'}|^2 = \frac{1 - w(\bar{n}) + 2w(\bar{n})\cos^2\phi}{2\pi |\delta(\gamma)| \sqrt{\varepsilon(\bar{n})}} \ , \quad (10)$$

where

$$\phi = \frac{1}{2}\delta(\gamma)\sqrt{2N+1} \ln\xi(\bar{n}) - \frac{\pi}{2}\Delta n - \frac{\pi}{4} \quad (11)$$

and

$$\xi(\bar{n}) = \frac{1 + \sqrt{1 - w(\bar{n})^2}}{1 - \sqrt{1 - w(\bar{n})^2}} \quad (12)$$

In Eq. (10) $\varepsilon(\bar{n})$ is given by

$$\varepsilon(\bar{n}) = \frac{1}{4}(2N+1)(1-w(\bar{n})^2) = \bar{n} + \frac{1}{2} - \frac{1}{2N+1}\left(\bar{n}+\frac{1}{2}\right)^2 \tag{13}$$

In other words, $\varepsilon(\bar{n})$ is $E_{\bar{n}}/\hbar\omega_e$ where E_n is the energy level of the Morse oscillator.

In the limit of large impact parameters the change in action is small, and the asymptotic expression for S matrix elements becomes invalid, since transition probabilities exceed unity. Cross section calculations call for taking into account contributions of all trajectories, thus the necessity arises of generalizing Eq. (10) to the case of small $\delta(\gamma)$. The derivation of the Bessel uniform approximation may be patterned after the method of Stine and Marcus [9]; however, in our case the desired result is conveniently obtained from simple intuitive considerations. For this purpose, consider the asymptotic expansions of the Bessel functions for large arguments

$$J_{\Delta n}^2(z) \approx \frac{2}{\pi z}\cos^2\left(z - \frac{\pi}{2}\Delta n - \frac{\pi}{4}\right),$$

$$J_{\Delta n}^2(z) + J_{\Delta n+1}^2(z) \approx \frac{2}{\pi z} \tag{14}$$

The analysis of formulae (10)-(14) obviously suggests that

$$|S_{nn'}|^2 = \frac{1-w(\bar{n})}{2}\left[J_{|\Delta n|}^2\left(2\delta(\gamma)\sqrt{\varepsilon(\bar{n})}\right) + J_{|\Delta n|+1}^2\left(2\delta(\gamma)\sqrt{\varepsilon(\bar{n})}\right)\right]$$

$$+ \frac{w(\bar{n})\ln\xi(\bar{n})}{2\sqrt{1-w(\bar{n})^2}} J_{|\Delta n|}^2\left(2\delta(\gamma)\sqrt{\varepsilon(\bar{n})}\frac{\ln\xi(\bar{n})}{2\sqrt{1-w(\bar{n})^2}}\right) \tag{15}$$

Dominant contribution to vibrational energy transfer probabilities near the dissociation limit is made by the first two terms, while the last term is the leading one in the limit of harmonic oscillator. Note that contributions from all three terms are comparable in magnitude for intermediate values of $w(\bar{n})$. Equation (15) is essentially simplified for the case of harmonic oscillator

$$|S_{nn'}|^2 = J_{|\Delta n|}^2\left(2\delta(\gamma)\sqrt{\bar{n}+1/2}\right) \tag{16}$$

The above expression was first derived by Clark and Dickinson [8] for collinear geometry of collisions. The quantity $<\delta^2(\gamma)>$ may be interpreted as the total energy (in units of $\hbar\omega_e$) transferred to a harmonic oscillator initially at rest [17].

In the present derivation we assume that the anisotropic interaction potential is strongly dominated by a single term of the Legendre polynomial expansion (usually $\lambda = 1$ or 2)

$$V(r,R,\gamma) = V(r)\exp(-R/L)\left[1 + qP_\lambda(\cos\gamma)\right] \ , \tag{17}$$

where q is the anisotropy parameter. With this potential, change in action (6) may be written as

$$\delta(\gamma) = A\big(b,v,\omega(\bar{n})\big)\left[1 + qP_\lambda(\cos\gamma)\right] \ , \tag{18}$$

where A depends on the impact parameter b, the relative velocity v and the mean transition frequency. These dependences are easily found in the case of rectilinear trajectory valid for $b \gg L$

$$A\big(b,v,\omega(\bar{n})\big) = \left(\frac{\hbar}{2M\omega_e}\right)^{1/2}\left(\frac{\partial V}{\partial r}\right)_e \frac{2L\alpha bK_1(\alpha b)}{\hbar v(\alpha L)^2} \tag{19}$$

Here $K_1(\alpha b)$ is the modified Bessel function of first order where α is defined as

$$\alpha = \frac{1}{L}\left[1 + \left(\frac{\omega(\bar{n})L}{v}\right)^2\right]^{1/2} \tag{20}$$

In another limiting case, an analytical determination of the head-on collision trajectory is also possible for the exponentially repulsive potential [1]

$$\exp\left[-\frac{R(t)}{L}\right] = \frac{\exp\left[-R(0)/L\right]}{\cosh^2(vt/2L)} = \frac{E}{V(r_e)\cosh^2(vt/2L)} \ , \tag{21}$$

where E is the initial kinetic energy. In the latter case we get

$$A\big(0,v,\omega(\bar{n})\big) = 2C_e\left(\frac{\mu vL}{\hbar}\right)\frac{\pi\omega(\bar{n})L/v}{\sinh[\pi\omega(\bar{n})L/v]} \ , \tag{22}$$

where μ is the reduced mass for the translational motion and the dimensionless parameter C_e is proportional to a logarithmic derivative

$$C_e = \left(\frac{\hbar}{2M\omega_e} \right)^{1/2} \frac{1}{V(r_e)} \left(\frac{\partial V}{\partial r} \right)_e \qquad (23)$$

The modified wave number approximation generalizes equation (22) to the case of impact parameters different from zero, and gives the explicit expression for vibrationally inelastic cross sections (see, for example, [1]). Unfortunately, this approximation has an essential defect. It is easily shown that for sudden collisions the inelastic cross sections have an oscillatory dependence on Δn, except for small A. Consequently, the behavior of the change in action with the impact parameter (at $b << L$) should be accurately defined by taking into account distant collisions. This is done using the following approximation

$$A\big(b, v, \omega(\bar{n})\big) = 2C_e \left(\frac{\mu v L}{\hbar} \right) \frac{\beta b \, K_1(\beta b)}{(\beta L)^2} \quad , \qquad (24)$$

where

$$\beta = \frac{1}{L} \left(\frac{\sinh[\pi\omega(\bar{n})L/v]}{\pi\omega(\bar{n})L/v} \right)^{1/2} \qquad (25)$$

At moderate values of the adiabatic parameter $\pi\omega L/v$, the modified expression (25) has the same functional dependence on $(\omega L/v)^2$ as expression (20) for α differing by the numerical factor $\pi^2/6$. Therefore, interpolation formula (24) contains both limiting cases thus providing the connection between them. True, the v dependence of the change in action has a discontinuity, but in that region of impact parameters where their contribution to inelastic cross-sections is not significant. Substituting equations (18) and (24) into (15) results in the analytical representation for transition probabilities depending on all parameters that define excitation (deactivation) of the Morse oscillator in collisions with atoms. Inelastic cross sections are

calculated numerically by integration over the impact parameter transition probabilities (4) as usual.

3. Results and discussion

The magnitude of the transition probability depends almost entirely on the parameter $\pi \omega L / v$. High values of this parameter indicate that collisions are adiabatic. This is a typical case for many molecules occupying low vibrational states. In this limit the change in action is exponentially small even for the trajectory with $b = 0$, so for small values of the Bessel function arguments we directly find

$$P_{nn'} \propto \exp\left[-\frac{2\pi \omega(\bar{n}) L \,|\, \Delta n\,|}{v} \right] = \exp\left[-\frac{2\pi L \,|\, E_{n'} - E_n \,|}{\hbar v} \right] \tag{26}$$

Symmetrization of the trajectory parameters, i.e., replacement of v by the mean velocity $(v + v')/2$ results in the transition probability being proportional to $\exp\left(-2\pi L \,|\, k - k' \,| \right)$ where k is the wave vector. Thus we relate our approach to the well-known result of Landau for exponentially repulsive potential [18].

Low values of $\pi \omega L / v$ are typical for sudden collisions, and this situation is particularly accurate for systems like He + I$_2$ in which a light atom interacts with a heavy molecule. In this case one can readily derive the energy dependence of vibrational excitation cross sections near the threshold where the relative velocity (v') after collision is small. This process is time-reversed relative to that where the initial velocity (v) is small. Using the principle of microscopic reversibility, we immediately find from Eqs. (15), (24)

$$\sigma_{nn'} \propto v'^{2\,|\Delta n|} \propto \left(E - E_{n'} + E_n \right)^{n'-n} \tag{27}$$

The excitation cross-sections $\sigma_{0 \to n}(E)$, which Hall *et al.* [19] measured in the region of the excitation threshold, demonstrate precisely such a behavior with energy.

The deviation from complete up-down symmetry can also be explained from Eq. (15). At fixed initial n and given Δn the mean quantum number $\bar{n}$ is greater for upward transitions

than for downward ones. As a consequence, the difference arises between the probabilities of T-V and V-T transitions due to the difference in adiabatic factors (see Eq. (8)). This is supported by experiments [20, 21].

As is seen from Eq. (24), the change in action is proportional to the reduced mass of colliding particles; moreover, it depends on the characteristic value of orbital angular momentum $\mu v L$. This dependence naturally accounts for isotopic effects in the crossed beams inelastic scattering of I_2 from H_2 and D_2 [20], as well as the difference in the behavior of cross sections with energy near the threshold for two targets He and D_2 [22].

Further conclusions are a trivial consequence of the Bessel function properties. First, a physical limitation on the maximum angular momentum transfer manifests itself in a rapid drop off of transition probabilities as a function of Δn beyond some characteristic value Δn^* such that $\Delta n^* \geq 2\delta(\gamma)\sqrt{\varepsilon(\overline{n})}$. Second, adiabatic effects result in the existence of classical dynamical threshold velocities for these large Δn collisions. Such effects depend crucially on the potential parameter L. So we conclude that dynamical rather than energetic constraints govern the collision process, a feature noted in the experiments by Krajnovich *et al*. [20,21].

Numerical calculations of inelastic cross sections show the following peculiarities. Transition probabilities averaged over all rotor orientations show an oscillatory dependence on Δn that is absent in cross sections calculated for fixed value of γ, i.e., integration over the impact parameter produces a monotonic dependence of σ on Δn for any orientation. The IOS approximation for the rotational degrees of freedom results in a weak dependence of cross sections on anisotropy parameters, though; in general, cross sections increase with increasing q. Calculations reported in this paper employ the potential parameters for I_2 + H_2 and D_2: $C_e = 0.1$, $L = 0.34$ Å and $q = 0$. These data were found by fitting experimental dependence of σ on Δn for I_2 + H_2 at the center-of-mass collision energy 89 meV [20]. With such an approach the anisotropy parameter was difficult to determine, thus we restricted ourselves to the contribution

from the isotropic part of the potential to vibrational energy transfer cross sections. Then, cross sections for the $I_2 + D_2$ system calculated at $E = 103$ meV were compared with experimental values [20] to test predictions of the theory. We used the spectroscopic parameters $\omega_e = 133.47$ cm^{-1} and $x_e = 0.0078$ found by fitting transition frequencies given in [20]. The results are shown in Fig.1. Note that at $E_{c.m.} \approx 220$ meV inelastic cross sections for $I_2 + H_2$ become equal in magnitude to the $I_2 + D_2$ cross sections at 103 meV, since the energy ratio $E_1 : E_2$ is approximately equal to the ratio $\mu_2 : \mu_1$ of reduced masses for isotopic targets in collisions with I_2. The reasons are as follows. Collisions are moderately non-adiabatic due to the low frequency of strongly anharmonic vibrations. Large values of the mean vibrational quantum number make the perturbation theory inapplicable in this case.

References

1. D. Rapp and T. Kassal, Chem. Rev. 69 (1969) 61.

2. S. Ormonde, Rev. Mod. Phys. 47 (1975) 193.

3. J.W. Duff and D.G. Truhlar, Chem. Phys. 9 (1975) 243.

4. A.P. Clark, A.S. Dickinson and D. Richards, Adv. Chem. Phys. 36 (1977) 63.

5. G.D. Billing, in: M. Capitelli (Ed.), Nonequilibrium Vibrational Kinetics, Springer-Verlag, Berlin, 1986. Chap. 4.

6. G.W. Flynn, C.S. Parmenter and A.M. Wodtke, J. Phys. Chem. 100 (1996) 12838.

7. C.E. Treanor, J. Chem. Phys. 43 (1965) 532.

8. A.P. Clark and A.S. Dickinson, J. Phys. B 4 (1971) L112.

9. J.R. Stine and R.A. Marcus, J. Chem. Phys. 59 (1973) 5145.

10. G.D. Billing, J. Chem. Phys. 62 (1975) 1480.

11. I.V. Adamovich and J.W. Rich, J. Chem. Phys. 109 (1998) 7711.

12. G.A. Parker and R.T Pack, J. Chem. Phys. 68 (1978) 1585.

13. P. Pechukas and J.C. Light, J. Chem. Phys. 44 (1966) 3897.

14. P.F. Naccache, J. Phys. B 5 (1972) 1308.

15. R.D. Levine, Chem. Phys. Lett. 95 (1983) 87.

16. W.H. Miller, Adv. Chem. Phys. 25 (1974) 69.

17. M.L. Strekalov, Khim. Fiz. (2002) in press.

18. L.D. Landau and E.M. Lifshitz, Quantum Mechanics, Addison-Wesley, Reading, 1958.

19. G. Hall, K. Liu, M.J. McAuliffe, C.F. Giese and W.R. Gentry, J. Chem. Phys. 81 (1984) 5577.

20. D.J. Krajnovich, K.W. Butz, H. Du and C.S. Parmenter, J. Phys. Chem. 92 (1988) 1388.

21. D.J. Krajnovich, K.W. Butz, H. Du and C.S. Parmenter, J. Chem. Phys. 91 (1989) 7725.

22. G. Hall, K. Liu, M.J. McAuliffe, C.F. Giese and W.R. Gentry, J. Chem. Phys. 84 (1986) 1402.

Figure captions

Fig. 1. Comparison of cross sections for vibrational relaxation of I_2^* (n = 35) by H_2 and D_2 from Ref. 20 with a theory and predictions based on the semiclassical model (Eqs. (15), (24)).