



ATOMIC-MOLECULAR COLLISIONS: ENERGY TRANSFER (Ar-N₂)

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1. ABSTRACT:

There has been a renewed effort, over the last few years, to develop reliable approximate descriptions of the molecular collision dynamics. One approach has been to reduce the number of equations, which are coupled together, and to retain the physically important couplings. Even with these reductions, the close coupling methods remain difficult in the determination of the inelastic cross sections. Another set of approximate methods has therefore, been developed which involve only the solution of uncoupled differential equations . The two most widely used methods of this latter type are the Exponential Distorted Wave (EDW) and the Infinite Order Sudden (IOS) approximations. The IOS is more reliable for low total angular momentum (J) quantum number whereas EDW is good for higher J values but is a more time consuming method. The relative role of the short and long-range anisotropies, kinematical factors and type of the transitions in determining the shape of the inelastic differential cross section have been analyzed in their work.

Key words: Exponential Distorted Wave (EDW), Infinite Order Sudden (IOS), close coupling (CC), generalized phase shift (GPS), generalized phase shift (CGPS), strong coupling correspondence principle (SCCP)

2. INTRODUCTION:

The interaction of an atom with a molecule introduces interesting physical phenomena, which have attracted experimental and theoretical interest (Bernstein, 1979; Buck, 1987; Faubel 1983 and Faubel and Kraft 1986). In the first place it is noted that the atom-molecular interaction depends on a number of additional parameters since in the Born-

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Oppenheimer limit it will depend on the orientation of the molecule with respect to the axis joining the centre of mass of the molecule with the instantaneous position of the atom as well as on all the intermolecular coordinates. Even for the simplest case of a diatomic molecule the potential given by $V(R, \theta, r)$ where θ is the angle between the axis of approach (R) and the bond distance (r) is a potential hypersurface. There are two types of potentials, 'the chemical' potential involving strong attractive exchange forces which hold molecules together and the much weaker but equally important 'Van der Waals' potentials involving weakly attractive London correlation forces (Fucchs *et al.*, 1984). These latter forces are important for understanding the properties of aggregate matter. Thus the Van der Waals forces determine the equations of state of a gas, liquid and solid and the phase transitions between these states. They also determine the kinetic properties such as the transport co-efficient.

3. FORMULAE & COMPUTATIONAL METHOD:

The energy transfer processes determine the rate at which equilibrium between the external (translational) and the internal molecular degrees of freedom is established. These processes are therefore of fundamental importance. Inelastic collisions also compete with radiative energy transfer and thus affect line width and line shifts and in some cases they determine the intensities of spectral lines. These processes have recently become of interest in laser technology, laser isotope separation and in interpreting the spectral lines of interstellar molecules. Lack of a more detailed knowledge of state-to-state inelastic rate constants is the greatest limiting factor in the advancement in all those areas.

The quantum mechanical close coupling (CC) as well as Distorted Wave approximations and CDEDW would be used to determine various quantities particularly the differential and the integral cross sections of interest regarding the above mentioned collision systems (Arthus and Dalgarno, 1960).

The potential for homonuclear diatom-inert gas atom systems is generally defined by -

$$V(\hat{R}, \hat{r}) = \sum_n V_n(\hat{R}) P_n(\hat{R} \cdot \hat{r}) \quad (n \text{ even})$$

where \hat{R} stands for the intermolecular position vector, \hat{r} gives the direction of the molecular axis and P_n is a Legendre polynomial of degree n . In fact, we only use terms with $n \leq 2$, thus $V(\hat{R}, \hat{r}) = V_0(\hat{R}) + V_2(\hat{R}) P_2(\hat{R} \cdot \hat{r})$. The angle between \hat{R} and \hat{r} will be denoted by θ , yielding $\cos\theta = \hat{R} \cdot \hat{r}$. Furthermore we choose the quantization axis parallel to the velocity vector of the incoming particle.

Starting from this potential, the CC Program yields the real K^J sub-matrices to which the T^J matrices are connected as follows:

$$T^J = -2iK^J \{I + K^J K^J\}^{-1} \{I + iK^J\}$$

The relation between the T^J and the S^J matrices is given by –

$$T^J = I - S^J$$

where I is the identity matrix.

The computer output yields the matrix elements for a fixed total energy E ; $E = E_{\text{kin}} + E_{\text{rot}} = \hbar^2 k_j^2 / 2\mu + B_j(j+1) = E'_{\text{kin}} + E'_{\text{rot}} = \hbar^2 k_j'^2 / 2\mu + B_j'(j' + 1)$, where quantities without (with) primes correspond to the situation before (after) the collision. The reduced mass of the system is indicated by μ . The total angular momentum number J is a good quantum number, i.e. there is no interaction between the different K^J , S^J or T^J sub-matrices. The rotational energy of the molecule before (after) the collision depends on the rotational quantum number j (j'), and the rotational constant B .

In DW approximations the S -matrix elements are given by -

$$S(l' m_l' j' m_j', l m_l j m_j) = (k_j / k_j')^{1/2} \exp[i(\eta_{lj} + \eta_{l'j'})] \\ \times \left[\delta_{jj'} \delta_{ll'} \delta_{m_j m_j'} \delta_{m_l m_l'} - \frac{4\mu i}{\hbar^2 k_j} \int_0^\infty F_{l'j'}(k_j' R) \left\langle j' m_l' l' m_l' \right| V_2(R) P_2(\hat{R} \bullet \hat{r}) \left| j m_j l m_l \right\rangle F_{lj}(k_j R) dR \right] \\ \text{---(4)}$$

Here, the functions $F_{lj}(R)$ ($F_{l'j'}(R)$) are solutions of the uncoupled Schrodinger equation, with $V(R) = V_0(R)$, corresponding to the kinetic energy before (after) the collision. The phase shifts η_{lj} and $\eta_{l'j'}$ are defined by the asymptotic behaviour $\lim_{R \rightarrow \infty} F_{lj}(R) \cong \sin(k_j R - l\pi/2 + \eta_{lj})$ and $\lim_{R \rightarrow \infty} F_{l'j'}(R) \cong \sin(k_j' R - l'\pi/2 + \eta_{l'j'})$, respectively. For our choice of quantization axis the potential matrix element is given by -

$$V_2(R) \left\langle j' m_l' l' m_l' \right| P_2(\hat{R} \bullet \hat{r}) \left| j m_j l m_l \right\rangle = V_2(R) \{ (2j+1)(2j'+1)(2l+1)(2l'+1) \}^{1/2} \\ \times (-1)^{m_j'} \begin{pmatrix} j' & 2 & j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & 2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & 2 & j \\ -m_j' & m_j' - m_j & m_j \end{pmatrix} \begin{pmatrix} l' & 2 & l \\ m_j - m_j' & m_j' - m_j & 0 \end{pmatrix} \delta_{m_l, 0} \delta_{m_l', m_j - m_j'} \\ \text{---(5)}$$

The quantum numbers $l, -l', m_j, m'_j, m_l, m'_l$ correspond with the orbital angular momentum before and after the collision, the projection of angular momentum j & j' and the projection of l & l' on the chosen quantization axis, respectively.

Starting from the scattering matrices scattering, amplitude is calculated. In CC we find

$$f(j'm'_j, jm_j, \chi) = \frac{1}{2} \frac{i}{(k_j k'_j)^{\frac{1}{2}}} (-)^{m_j - m'_j} e^{i(m_j - m'_j)\varphi} \sum_{J=0}^{\infty} \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} i^{l-l'} \begin{pmatrix} l & j & J \\ 0 & m_j & -m_j \end{pmatrix} \begin{pmatrix} l' & j' & J \\ m_j - m'_j & m'_j & -m_j \end{pmatrix} \\ \times (2J+1) \left\{ \frac{[l' - (m_j - m'_j)]!}{[l' + (m_j - m'_j)]!} \right\}^{\frac{1}{2}} [(2l+1)(2l'+1)]^{\frac{1}{2}} P_l^{m_j - m'_j}(\cos \chi) T^J(j'l', jl) \quad \text{-----}(6)$$

Associated Legendre polynomials are denoted by $P_l^{m_j - m'_j}(\cos \chi)$ (Edmonds, 1957), where χ corresponds to the deflection angle i.e. the angle between \hat{k} and \hat{k}'_j , the unit wave vectors of the incoming and outgoing particle, respectively. The azimuth angle φ determines for $\varphi = 0$ the plane of scattering. With the help of eq. (4), the analogue formula in DW approximations is derived as

$$f(j'm'_j, jm_j, \chi) = -\frac{i}{2k_j} \sum_{l=0}^{\infty} (2l+1) [\exp(2i\eta_{lj}) - 1] P_l(\cos \chi) \delta_{jj'} \delta_{m_j m'_j} \\ - \frac{2\mu}{\hbar^2 k_j k'_j} (-)^{m_j - m'_j} e^{i(m_j - m'_j)\varphi} \sum_{l=0}^{\infty} \sum_{l'=0}^{\infty} i^{l-l'} [(2l+1)(2l'+1)]^{\frac{1}{2}} \left\{ \frac{[l' - (m_j - m'_j)]!}{[l' + (m_j - m'_j)]!} \right\}^{\frac{1}{2}} \\ \times P_l^{m_j - m'_j}(\cos \chi) \int_0^{\infty} F_{l'j'}(k'_j R) V_2(R) F_{lj}(k_j R) dR \left\langle j'm'_j l' m'_l \left| P_2(\hat{R} \cdot \hat{r}) \right| j m_j l m_l \right\rangle \exp[i(\eta_{lj} + \eta_{l'j'})] \\ \text{----- (7)}$$

The matrix element $\langle j'm'_j l' m'_l | P_2(\hat{R} \cdot \hat{r}) | j m_j l m_l \rangle$ determines the selection rules in DW approximations:

$$j' = j, j \pm 2; l' = l, l \pm 2; m'_j = m_j, m_j \pm 1, m_j \pm 2; m_l = m_j + m_l = m'_j + m'_l$$

For the integral cross-section one finds in CC.

$$\sigma(j'm'_j, jm_j) = \frac{k'_j}{k_j} \int |f(j'm'_j, jm_j, \chi)|^2 d\Omega$$

$$= \frac{\pi}{k_j^2} \sum_{l'=0}^{\infty} \left| \sum_{J=|l'-j'|}^{l'+j'} \sum_{l=|J-j'|}^{J+j'} i^{l-l'} \begin{pmatrix} l & j & J \\ 0 & m_j & -m_j \end{pmatrix} \begin{pmatrix} l' & j' & J \\ m_j - m'_j & m'_j & -m_j \end{pmatrix} (2J+1)(2l+1)^{1/2} T^J(j'l', jl) \right|^2 \quad \text{---}$$

------(8)

and similarly, in DW approximations

$$\sigma(j'm'_j, jm_j) = \frac{16\pi\mu^2}{\hbar^4 k_j^3} (2j+1)(2j'+1) \begin{pmatrix} j' & 2 & j \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j' & 2 & j \\ -m'_j & m'_j - m_j & m_j \end{pmatrix}^2 \sum_{l'=0}^{\infty} (2l'+1)$$

$$\times \left\{ \left| \sum_{l=0}^{\infty} i^{l-l'} (2l+1) \begin{pmatrix} l' & 2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & 2 & l \\ m'_j - m_j & m_j - m'_j & 0 \end{pmatrix} \int_0^{\infty} F_{l'j'}(k'_j R) V_2(R) F_{lj}(k_j R) dR \cos(\eta_{lj} + \eta_{l'j'}) \right|^2 \right.$$

$$\left. \left| \sum_{l=0}^{\infty} i^{l-l'} (2l+1) \begin{pmatrix} l' & 2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & 2 & l \\ m'_j - m_j & m_j - m'_j & 0 \end{pmatrix} \int_0^{\infty} F_{l'j'}(k'_j R) V_2(R) F_{lj}(k_j R) dR \sin(\eta_{lj} + \eta_{l'j'}) \right|^2 \right\}$$

------(9)

In general, the differential cross section is related to the scattering amplitude by:

$$d\sigma(j'm'_j, jm_j, \chi) / d\Omega = (k'_j / k_j) |f(j'm'_j, jm_j, \chi)|^2 \quad \text{---(10)}$$

The total integral, degeneracy averaged, cross section given by -

$$\bar{\sigma}(j', j) = \frac{1}{2j+1} \sum_{m_j m'_j} \sigma(j'm'_j, jm_j) = \frac{\pi}{k_j^2} \sum_J \frac{2J+1}{2j+1} \sum_{ll'} |\delta_{jj'} \delta_{ll'} - S^J(j'l', jl)|^2 \quad \text{---(11)}$$

The definition of the relaxation cross section is taken from Schafer and Gordon 1973.

$$\sigma^k(j'j', jj) = \frac{\pi}{k_j^2} \sum_{J\alpha J\beta ll'} [(2j'+1)/(2j+1)]^{1/2} (2J_\alpha+1)(2J_\beta+1) \left\{ \begin{matrix} j' & k & j' \\ J_\beta & l' & J_\alpha \end{matrix} \right\} \left\{ \begin{matrix} j & k & j \\ J_\beta & l & J_\alpha \end{matrix} \right\}$$

$$\times [\delta_{jj'} \delta_{ll'} - S^{J_\beta}(j'l', jl) S^{J_\alpha}(j'l', jl)] \quad \text{-----(12)}$$

Here, spin rotational relaxation corresponds to k = 1 spin coupling relaxation to k = 2.

The opacity function $P^J(j', j)$ with $j' \neq j$ is defined by -

$$P^J(j', j) = \frac{k_j^2}{\pi} \frac{1}{2J+1} \bar{\sigma}^J(j', j) = \frac{1}{2j+1} \sum_{ll'} |S^J(j'l', jl)|^2 \quad \text{-----(13)}$$

where $\bar{\sigma}^J(j', j)$ is the contribution to $\bar{\sigma}(j', j)$ of the partial waves belonging to the total angular momentum quantum number J one has

$$P^J(j', j) = \frac{k_j^2}{\pi} \frac{1}{2J+1} \bar{\sigma}^J(j', j) = \frac{1}{2j+1} \sum_{ll'} |S^J(j'l', jl)|^2 \leq 1$$

i.e. $P^J(j', j)$ can assume unity only for completely inelastic, events. For dominant coupling (i.e. if all channels receive an equal share of probability) one finds $P^J = (2j' + 1) / N$, where N equals the total number of open channels, If energetically only $j' = 1$ and 3 is allowed, $N = 10$, for instance, excitation of $j = 1$ to $j' = 3$ would yield them $P^J(j', j) = 7/10$.

The rotational-translational energy transfer in collisions between N₂ and noble-gas atoms has been investigated experimentally as well as theoretically by (Kistemaker *et al.* 1975). Experimental relaxation times have been derived from acoustical absorption measurements. These experimental observations are confirmed by classical trajectory calculations using a dumbbell model for the intermolecular potential.

(Pack 1975) have done an accurate quantum mechanical close-coupling (CC) calculations and integral cross sections are reported for rotationally inelastic scattering at room temperature using an empirical intermolecular potential. These cross sections are used to test the infinite order sudden (IOS) approximation along with several other models [classical trajectories (CT) full sudden (SA) generalized phase shift (GPS) and classical limit generalized phase shift (CGPS)]. The CT method works well for all the cross sections examined.

(De Pristo and Alexander 1975) using an L-dominant technique have simplified the close-coupled equations for collisions between atoms and diatomic molecules. The scattering cross sections have been calculated and compared with the CC, EP and CS results. It has been noticed that the L-dominant (LD) method is more accurate than other methods. Further, it is more accurate in those cases where the total angular momentum (J) values are larger. The method is found to be comparatively faster than other approximations.

(Dickinson and Richards 1976) have tested the utility of the strong coupling correspondence principle approximation (Percival and Richards 1970) and found it to be an accurate one and time saving particularly, in more complex systems where comparatively higher number of J values are involved.

(Shapiro and Tamir 1976) have determined the rotational excitations cross section using the p-helicity (projection of J on the body fixed axis) decoupling approximation. The results agree reasonably well with those available from molecular beam scattering

experiments. The relative role of the short and long-range anisotropies, kinematical factors and type of the transitions in determining the shape of the inelastic differential cross section have been analyzed in their work.

(Pattengil and Bernstein 1976) have done the surprisal analysis of the classical trajectory calculation of rotationally inelastic cross sections and have discussed in detail about the influence of the potential energy surfaces. (Pattengil 1977) in his latter work explored the use of the body fixed coordinates in classical scattering calculations. The planer trajectory approximation is the one such method, which has been shown to yield accurate cross sections for rotationally inelastic scattering. The planer cross sections are nearly equal to the CC results and takes only one third of the computer time to that of CC calculation. (Dickinson and Richards 1977) have done a semi-classical study for rotational excitation in atom molecule collisions using the body fixed coordinates. They found that the strong coupling correspondence principle (SCCP) approximation is similar to the coupled state (CS) approximation and have shown that the SCCP approximation is a successful method.

The Aziz-mod potential showed the best agreement with the measurements. Compared with the PLBC potential, the well of the Aziz-mod potential is deeper, potential (Pack 1978), called VAN, to his measured rainbow structure. The anisotropies in a LJ potential form (Van den Biesen *et al.* 1982) and well depth of the VAN potential lie between those of PLBC and KDV potentials while the minimum occurs at smaller separations than for any of the other potentials described above.

(Brunetti *et al.* 1983) obtained two spherically averaged potentials from an analysis of the absolute total cross sections measured by the molecular beam technique. They fitted these to a Simons-Parr-Finlan-Dynham potential (Simons *et al.* 1973) and an exponential-spline-Morse-Spline- Van der Waals potential (Pirani and Vecchiocattivi 1981).

The data available so far are insufficient to determine a full potential surface. Therefore the potential of Pattengil *et al.* (1971) has been used in the present study.

$$V(R, \theta) = 4\epsilon\{(\sigma/R)^{12} [1 + b_2 P_2(\cos\theta)] - (\sigma/R)^6 [1 + a_2 P_2(\cos\theta)]\}$$

a_2 and b_2 are the attractive and repulsive anisotropy parameters.

4. CONCLUSION:

The accuracy of the various CDWD cross sections as obtained in the present calculations has been examined in the light of the results of the close-coupling (CC) and coupled state (CS) time dependent perturbation, semi-classical version of the IOS approximation (SIOS), discrete sudden perturbation theory (DSPT) and semi-classical sudden perturbation theory (SSPT)

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