DISTORTED WAVE CALCULATIONS OF THE VIBRATIONAL RELAXATION OF CO IN COLLISION WITH He ATOMS

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Cross sections are calculated for vibrational relaxation of the CO/He system. The calculations use the exponential distorted wave, the distorted wave and close-coupling techniques for the vibrational motion. Rotational motion is treated with the infinite-order sudden approximation. Good agreement is shown between the distorted wave methods and the close-coupled calculations. Vibrational relaxation rate constants are calculated and compared with experimentally determined values. The distorted wave approximation is shown to provide results of useful accuracy.

1. Introduction

Quantum mechanical studies of the change of vibrational energy in molecule–atom and molecule–molecule collisions in the gas phase are limited by the large mathematical dimensionality of the problem [1]. A major source of this dimensionality is the number of rotational states which, at the energies of vibrational relaxation, are necessary for converged calculations. Consequently the full problem of vibrational relaxation can in practice only be solved for the interactions of hydrogen with structureless particles.

Several approximate methods have been developed to permit the computation of vibrationally inelastic collision cross sections. These include the coupled-states (CS) [2–4] and the infinite-order sudden (IOS) [5–13] approximations. The latter has been used to study vibrational relaxation in linear triatomic molecule–atom [7], non-linear triatomic molecule–atom [12] and symmetric top molecule–atom [13] collisions. These studies have used the IOS for rotational motion and a vibrational close-coupled (VCC) technique for vibrational motion. The VCC IOS calculations treat vibrational motion, within the Born–Oppenheimer approximation, exactly. It is difficult to extend such studies to higher energies and more complex molecules because of the number of vibrational channels. These increase, extremely rapidly for polyatomic molecules, with an increase in the energy. Therefore other, more approximate, methods are necessary to deal with this dimensionality problem.

The distorted wave (DW) and exponential distorted wave (EDW) approximations offer possible solutions to this problem. The DW approximation has been used in combination with a number of other approximations to form the Schwartz–Slawsky–Herzfeld (SSH) theory of vibrational energy transfer [14]. However, because of the large number of approximations upon which this theory is built, the agreement both with experiment and with more sophisticated calculations can at the best only be qualitative [15]. Therefore SSH theory does not provide a test of the DW approximation.

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A considerably more sophisticated method is produced by combining the EDW and IOS approximation. The resultant method, the EDW IOS approximation, has been compared with VCC IOS calculations for I₂/He [16] and, in modified form, for H₂/He [17] collisions. These studies both showed that the agreement was very close. More recently [18], calculations on the CO₂/He and CO₂/Ar systems have yielded slightly less satisfactory comparisons, but nevertheless confirm the utility of the EDW IOS procedure. It is the intention of this paper to compare EDW IOS and DW IOS with VCC IOS calculations for CO/He collisions so as to examine the accuracy and applicability of the distorted wave approximations.

There is a variety of reasons for choosing CO₂/He for this study. Firstly, the use of the IOS has been tested for this system [8–10]. Secondly, there exists an accurate potential energy surface calculated using a method which included electron-correlation (SCF CI) [8,19]. As this surface exists for both equilibrium and non-equilibrium values of the CO vibrational coordinate it contains all the information necessary for the calculation of vibrational relaxation in CO/He collisions. It is one of the very few accurately computed potentials which include the vibrational-coordinate dependence.

2. Scattering calculations

2.1. The infinite-order sudden approximation

The basis of the IOS approximation is that the close-coupled radial equations of the scattering problem

\[ \frac{d^2}{dr^2} + k_e^2 + \frac{L(L+1)}{R^2} \] U_{o',o}(R; \gamma)

\[ - \sum_{o''} V_{o',o''}(R; \gamma) U_{o'',o}(R; \gamma), \]

(1)

are solved for fixed angles \( \gamma \) [20–22]. Here \( \gamma \) is the angle between the vector \( \mathbf{r} \) along the diatom molecular axis and the vector \( \mathbf{R} \) from the atom to the diatom centre of mass. The prime denotes the quantum state after the collision. The matrix elements \( V_{o',o}(R; \gamma) \), of the interaction potential at fixed, \( \gamma \), are given by

\[ V_{o',o}(R; \gamma) = \langle 2\mu/\hbar^2 \rangle \langle v | V(R, r; \gamma) | v' \rangle, \]

(2)

where \( |v\rangle \) is the vibrational eigenstate of the diatomic molecule with quantum number \( v \) and \( \mu \) is the reduced mass of the diatom/atom system. The elements of the diagonal matrix \( k_e^2 \) are given by

\[ k_e^2 = (2\mu/\hbar^2)(E - \epsilon_v), \]

(3)

where \( \epsilon_v \) is the energy of the vibrational state with quantum number \( v \) and \( E \) is the total energy.

The equations (1) are solved subject to the boundary conditions

\[ \lim_{R \to \infty} U_{o',o}^L(R; \gamma) \]

\[ = \exp[-i(k_o R - L\pi/2)] \delta_{o',o} \]

\[ - (k_o/k_{e'})^{1/2} S_{o',o}^L(\gamma) \times \exp[i(k_{e'} R - L\pi/2)], \]

(4)

at large internuclear separations. The \( S \) matrix which results from the calculations will be unitary and symmetric [1,25]. The total cross sections can now be calculated by integration over \( \gamma \) [20–22]

\[ \sigma_{o',o} = \int \sigma_{o',o}(\gamma) \sin \gamma \, d\gamma, \]

where

\[ \sigma_{o',o}(\gamma) = (\pi/2k_e^2) \sum_L (2L + 1)|S_{o',o}^L(\gamma) - \delta_{o',o}|^2. \]

(5)

2.2. The vibrational close-coupling technique

The VCC IOS technique requires that the radial equations (1) be solved exactly as a set of coupled differential equations [6,7]. There is a number of methods for carrying this out [1]. The calculations in this paper have used the \( R \) matrix propagator technique [24]. The algorithm for this has been adapted from Clary's programmes for CO₂/He vibrationally inelastic scattering. The \( R \) matrix

\[ \text{Note that an adiabatic distorted wave approach was used in ref. [17].} \]
propagator method combines accuracy and speed in simple algorithms to calculate the $S$ matrices.

2.3. The distorted wave approximation

The DW approximation is a perturbation method which involves the truncation of the distorted wave series for the radial functions $U_{v', v}(R)$ [25]. This series is formed by repeatedly substituting for the exact radial wavefunction $U_{v', v}(R)$ in the right-hand side of the integral equation

$$U_{v', v}(R) = w_{v'}^1(R)\delta_{v', v} + \int_0^\infty G_{v'}^L(R, R') \times \sum_{v'' \neq v'} V_{v', v''}(R')U_{v', v''}(R') dR',$$

where the Green function is given by

$$G_{v'}^L(R, R') = -k_v^{-1}w_{v'}^2(R_g)w_{v'}^1(R_s),$$

and $R_g$ and $R_s$ are respectively the greater and smaller of $R$ and $R'$. The Green function is defined in terms of the solutions to the elastic scattering problem [25]

$$\frac{d^2}{dR^2} + k_v^2(L + 1/R^2) w_{v'}^L(R) = V_{v', v}(R) w_{v'}^L(R),$$

which have boundary conditions

$$\lim_{R \to \infty} w_{v'}^L = \sin \left[k_v(R) - L \pi/2 + \eta_v', v \right],$$

$$\lim_{R \to \infty} w_{v'}^L = \exp \left[-i \left[k_v(R) - L \pi/2 + \eta_v', v \right] \right].$$

The distorted wave approximation to the $S$ matrix is

$$S_{v', v}^L = \exp(i\eta_{v'}) \left[\delta_{v', v} + iA_{v', v}^L \right] \exp(i\eta_{v'}),$$

where the $A$ matrix elements are given by

$$A_{v', v}^L = 0, \quad v' = v;$$

$$A_{v', v}^L = -\left[2/(k_v k_{v'})^{1/2}\right] \int_0^\infty w_{v'}^L(R) \times \sum_{v'' \neq v} V_{v', v''}(R) w_{v'}^L dR', \quad v' \neq v.$$

One disadvantage of the $S$ matrix which results is that it will not necessarily be unitary. This lack of unitarity, which is a sign of unrealistic behaviour, will be more marked when the off-diagonal elements are comparable in magnitude to the diagonal elements. The problem can be overcome by the use of the exponential distorted wave (EDW) approximation [23, 25]. In this approximation the $S$ matrix is given by

$$S_{v', v}^L = \exp(i\eta_{v'}) \left[\exp(iA^L) \right]_{v', v} \exp(i\eta_{v'}),$$

and is always unitary. The method may be viewed as a partial resummation of the distorted wave series and is thus more accurate than the DW approximation. The disadvantage of the EDW approximation is that it is necessary to calculate all the elements of the $A$ matrix to obtain a single cross section or rate constant for a process from one quantum state to another. Therefore for a large number of channels the EDW approximation will require more time than the DW approximation; it will however still have considerable computational advantage over a VCC calculation.

The programme which carried out these distorted wave calculations is slightly different from that used for the EDW IOS and DW IOS calculations reported in ref. [16]. The differences is that in the latter algorithm a variable step size was used for the calculation of the distorted waves. In the present work a fixed step size is used. This was found to be necessary to obtain converged cross sections. This was attributed to the fact that the variable step algorithm interpolated the potential whereas the fixed step size programme calculated the potential, with the aid of eqs. (13) and (14), at the necessary points. The interpolation is particularly a problem for CO/He which has such small cross sections. The method for solving the elastic problem and calculating the distorted wave integrals is exactly the same for both this work and ref. [16].

3. The intermolecular potential and vibrational wavefunctions

The intermolecular potential used in these calculations is the SCF CI surface published by Thomas et al. [19] and Schinke and Diercksen [8].
This exists in the form of a series of points over a grid of values of $R$, $r$ and $\gamma$. In the present paper the value of the potential for arbitrary $R$, $r$ and $\gamma$ has been computed by fitting a function in $R$ for a fixed set of $r$ and $\gamma$ and then interpolating in $r$ and $\gamma$ with the expression

$$V(R, r, \gamma) = \sum_{\lambda=0}^{6} \sum_{k=0}^{2} V_{\lambda}^{k}(R) P_{\lambda} \cos(\gamma)(r - r_{eq})^{k}. \quad (13)$$

For fixed values of $r$ and $\gamma$, the functional form in $R$ is taken to be similar to that suggested by Huxley et al. [26]

$$V(R, r, \gamma) = (a_{1} + a_{2}r + a_{3}r^{2} + a_{4}r^{3}) \exp(-a_{5}R)$$

$$- \tanh(R - R_{\text{min}}/2)$$

$$\times (a_{6}/R^{6} + a_{7}/R^{7} + a_{8}R^{8}). \quad (14)$$

The coefficients $a_{1}$ to $a_{4}$ have been determined by fitting to the potential points. The coefficients $a_{5}$ to $a_{8}$ have been taken as the correct asymptotic multipole interactions given by Parker and Pack [27]. All the parameters are listed in Table 1 for each of the fixed values of $r$ and $\gamma$. These parameters enable us to evaluate the potential over the grid of $(r, \gamma)$ values at any desired value of $R$ (i.e. $R'$). These eighteen values of $V(R', r, \gamma)$ allow us to substitute into eq. (13) and solve the resulting set of simultaneous equations for the $V_{\lambda}^{k}(R')$ coefficients. This then provides an analytic fit to the potential for all values of $r$ and $\gamma$ at the selected value of $R = R'$. It should be noted that the analytic fit just described differs from that of Schinke and Diercksen [8]. The full SCF CI results have been used to determine parameters $a_{1}$ through $a_{5}$, while the long-range part of the potential is taken from the best available experimental data. In the analytic

<table>
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<td>0.5074</td>
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<td>231.7</td>
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</table>

$R_{\text{min}}$: 8.517, 7.954, 7.178, 6.742, 6.748, 6.877, 7.132

*All units atomic units; $AEB = A \times 10^{B}$.*
fit of ref. [8], the SCF CI calculations were used only to determine the vibrationally elastic (i.e. with \( k = 0 \)) part of the potential. The vibrationally inelastic parts \( (k \neq 0) \) were determined with an SCF potential.

The diatomic vibrational wavefunctions were represented as Morse oscillator wavefunctions [28] with the parameters \( D_e = 11.243 \) eV, \( r_{eq} = 1.1283 \) Å and \( \alpha = 2.298 \) Å\(^{-1} \). These parameters give excellent agreement with the CO vibrational energies given in standard texts [29].

4. Results and discussion

Cross sections for the vibrational deactivation process \( v = 1 \rightarrow v = 0 \) have been calculated for the CO/\(^4\)He and CO/\(^3\)He systems over the collision energy range 0.005–1.0 eV. The cross section changes by over six orders of magnitude across this range. Three different types of calculations were performed: VCC IOS, EDW IOS and DW IOS. The VCC IOS calculations used 300 \( R \) matrix sectors and a basis of up to seven vibrational states of CO. This set was chosen so as to always include two closed channels. For the EDW IOS method all open vibrational channels were included, i.e. from 2 at the lowest energies to 5 at the highest. The distorted waves were calculated for 1500 equally spaced points. For all calculations eight orientations were averaged to obtain the IOS cross sections.

The calculated cross sections are listed in tables 2 and 3 for CO/\(^4\)He and CO/\(^3\)He collisions respectively. Except at the highest energies, where the agreement is still extremely close, the EDW IOS and DW IOS results are identical for both collision systems. This similarity indicates that the breakdown of unitarity in the \( S \) matrix is negligible. Therefore it would be sufficient to use the computationally cheaper DW IOS procedure for either system in the energy range studied.

The final column in tables 2 and 3 shows the ratio of the \( v = 1 \rightarrow v = 0 \) vibrational relaxation cross sections as calculated using the EDW IOS and VCC IOS procedures. It is seen immediately that the distorted wave approximation is more valid for the lighter of the two collisions partners.

### Table 2

<table>
<thead>
<tr>
<th>Kinetic energy</th>
<th>VCC</th>
<th>DW</th>
<th>EDW</th>
<th>EDW/VCC</th>
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<td>5</td>
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<td>1.58(−9)</td>
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<td>1.20</td>
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<tr>
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<td>2.62(−2)</td>
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</tbody>
</table>

**a)** Energy in meV and cross sections in \( \text{Å}^2 \).

For CO/\(^3\)He the errors arising from the use of the exponential distorted wave approximation are between 11% and 14% while for the heavier CO/\(^4\)He system they lie between 19% and 21%. Calculations which are valid to this degree of accuracy are of considerable utility in this field, even for quantitative purposes. For the consideration of propensity rules and general trends, the accuracy achieved here is completely adequate.

It is interesting to compare the cross sections obtained here with those calculated in refs. [8,9]. As previously pointed out, the potential used in

### Table 3

<table>
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<tr>
<th>Kinetic energy</th>
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</table>

**a)** Energy in meV and cross sections in \( \text{Å}^2 \).
the present work differs from that of ref. [8]. At the lowest energies the present calculations predict smaller cross sections for both collision partners. These cross sections, however increase faster with energy than do those of ref. [8] and soon overtake them in magnitude. The cross sections for CO/\(^4\)He vibrational relaxation calculated by Banks and Clary [9], with the VCC IOS approximation, are smaller than these reported here. At 0.01 eV they are about half the magnitude of these while at 0.2 eV they are lower by 6%.

The disparity between the cross sections reported in tables 2 and 3 and those of refs. [8,9] arises from the differences in the analytic form of the potentials used. In the work of Schinke and Diercksen [8], a comparison is made of IOS and CS calculations for the CO/He system. They conclude, that for both He isotopes, the IOS approximation leads to an underestimate of the cross sections. At the energy of 0.1 eV this error is in the region of 20%. Banks and Clary [9] also comparing the CS and IOS approximation for a more approximate potential show differences with the IOS still underestimating the CS cross sections but by a larger amount. At an energy of 0.1 eV they show IOS results which are half those of the CS. Tables 2 and 3 show the DW approximation consistently predicts overly large cross sections. The two errors, therefore, are in opposed directions and to some extent cancel each other out.

In fig. 1 vibrational relaxation rate constants, calculated from the VCC IOS cross sections, are compared with experimental ones [10,15], while in fig. 2 a similar comparison is shown for rate constants derived from the DW IOS cross sections. The agreement with experiment is seen to be good, becoming progressively better with increasing temperature. On the scale shown, the differences between the VCC IOS and DS IOS rate constants would not be discernible. The agreement of the present calculations with the experiment is better than that in ref. [8] and considerably better than in ref. [9]. The cause of this is almost certainly the difference in the analytic potential used.
In ref. [10] IOS rate constants are calculated for a very wide range of isotopes and temperatures. There are compared with experimental and good agreement is shown. The potential is identical with that used in the work reported here. This agreement gives evidence for the accuracy of both this potential and the IOS for CO/He.

5. Conclusions

Approximate, and computationally simpler, DW IOS and EDW IOS methods have been tested against VCC IOS calculations for the vibrational relaxation cross sections of the isotopes of He with CO. The simpler calculations have been shown to give reliable results which can provide a useful basis for comparison with experiment. The calculations reported here, and comparison with other work, bring out two interesting points:

(1) the great sensitivity of vibrational cross sections to fine details of the potentials used, and

(2) the greater accuracy of the distorted wave approximation when applied to lighter collision partners.

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