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Method for the determination of parametric potential energy surfaces by the direct inversion of inelastic scattering data

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A direct method is described for inverting inelastic scattering data to obtain parameters in potential energy surfaces. A scattering perturbation technique is adapted to obtain a set of equations for the parameters. These equations are solved iteratively by a repeated solution of the close-coupled equations. The technique is used to determine C_6 coefficients in pair potentials for He + CH_3F by inverting experimental vibrational relaxation rate constant data. The azimuthal and vibrational close-coupling, rotational infinite-order sudden method is used in these computations.

I. INTRODUCTION

The inversion of experimental atom–atom elastic scattering data to determine potential energy functions is a routine procedure.[1] There are no general and direct methods, however, that have been formulated to invert molecular inelastic scattering information to obtain potential energy surfaces. This is despite the fact that a rich body of rotationally and vibrationally inelastic scattering data is being accumulated using a variety of experimental techniques.[2] A "distorted-wave peeling" method has been proposed[3] which, in special circumstances, can invert rotationally inelastic differential cross sections to yield numerical potentials for atom–diatomic molecule collisions. However, for most polyatomic problems, a much more useful form of potential is one in a functional form that contains parameters which can be varied to fit experimental data. An ideal would be a direct technique capable of determining these potential parameters from experimental data without resorting to least-squares optimization techniques; these are usually inefficient for this type of problem and can have convergence difficulties.

In this paper, we describe a direct approach for inverting inelastic scattering cross sections to obtain parameters in potential energy surfaces. The method is based on writing S matrix elements in an integral equation form so that a set of equations can be established for determining the potential parameters. Convergence on the parameters is achieved iteratively by a procedure which involves repeated solution of coupled-channel equations. The technique can be used to invert all kinds of inelastic scattering data, including vibrational-rotational integral and differential cross sections, rate constants and other scattering properties that require the evaluation of S matrix elements.

We apply the method to the inversion of an experimental[4] rate constant for the vibrational relaxation of CH_3F in collisions with He atoms. The azimuthal and vibrational close-coupling, rotational infinite-order sudden (AVCC-IOS) method[5] is used in the computations. The potential for He + CH_3F is assumed to take a pairwise form, and the inversion method is used to determine a C_6 coefficient in the pair potentials.

Secion II gives a general description of the inversion method. The incorporation of this method into the AVCC-IOS theory is described in Sec. III and the application to the inversion of an experimental vibrational relaxation rate constant for He + CH_3F is described in Sec. IV. Conclusions are in Sec. V.

II. INVERSION METHOD

For a molecular collisional system with center-of-mass distance vector $\mathbf{R}$ and internal molecular coordinates denoted by $\mathbf{Q}$, the Hamiltonian can be written as

$$H(\mathbf{R},\mathbf{Q}) = H_0(\mathbf{R},\mathbf{Q}) + \sum_m c_m V_m(R,\mathbf{Q}), \qquad (1)$$

where

$$H_0(\mathbf{R},\mathbf{Q}) = N_0(\mathbf{R},\mathbf{Q}) + V_0(R,\mathbf{Q}). \qquad (2)$$

In Eq. (1), $\{c_m\}$ are the linear coefficients of the interaction potential that are to be determined by inverting experimental inelastic scattering data. $N_0(\mathbf{R},\mathbf{Q})$ contains all kinetic energy operators together with the internal potentials of the isolated molecules before collision. Both the potentials $V_0(R,\mathbf{Q})$ and $V_m(R,\mathbf{Q})$ tend to zero as R tends to infinity.

The wave function which satisfies

$$H_0(\mathbf{R},\mathbf{Q})\psi_0^J(\mathbf{R},\mathbf{Q}) = E\psi_0^J(\mathbf{R},\mathbf{Q}), \qquad (3)$$

where E is the total energy and J is the total angular momentum, can be written in the coupled-channel (CC) form

$$\psi_0^J(\mathbf{R},\mathbf{Q}) = \sum_n g_{nJ}^0(R)h_n(\hat{R},\mathbf{Q}). \qquad (4)$$

Here, h_n is a basis function for asymptotic quantum state n and g_{nJ}^0 is a "translational" function which satisfies, for $J = 0$,

$$\left[\frac{d^2}{dR^2} + k_n^2\right]g_{nJ}^0(R)$$

$$= \frac{2\mu}{\hbar^2}\sum_{n'}V_{0nn'}(R)g_{n'J}^0(R), \qquad (5)$$

where

$$V_{0nn'}(R) = \langle h_n(\hat{R},\mathbf{Q})|V_0(R,\mathbf{Q})|h_{n'}(\hat{R},\mathbf{Q})\rangle. \qquad (6)$$

Here, k_n is the wave number for initial internal level n, and μ is the collisional reduced mass. The g functions satisfy the boundary conditions

$$g_{n'J}^0(R) \xrightarrow{R \to 0} 0,$$

$$g_{n'J}^0(R) \xrightarrow{R \to \infty} (k_{n'})^{-1/2}\{\delta_{nn'} \exp[-i(k_n R - J\pi/2)]$$

$$- S_{n'n}^{J0} \exp[i(k_{n'}R - J\pi/2))]\,, \tag{7}$$

where $S_{n'n}^{J0}$ is an S matrix element.

Similarly, the wave function which satisfies

$$H(\mathbf{R},\mathbf{Q})\psi^J(\mathbf{R},\mathbf{Q}) = E\psi^J(\mathbf{R},\mathbf{Q}) \tag{8}$$

can be expressed as

$$\psi^J(\mathbf{R},\mathbf{Q}) = \sum_n g_{nJ}(R)h_n(\hat{R},\mathbf{Q}), \tag{9}$$

and an S matrix element $S_{n'n}^J$ is obtained by applying boundary conditions analogous to those used for $g_{n'J}^0(R)$.

It is then possible to express $\mathbf{S}^J$ in first-order perturbation form

$$\mathbf{S}^J = \mathbf{S}^{J0} + \frac{i}{2}\sum_m c_m \mathbf{U}_m, \tag{10}$$

where

$$\mathbf{U}_m = \frac{2\mu}{\hbar^2}\int_0^\infty [\mathbf{g}_J^0(R)]^T \mathbf{V}_m(R)\mathbf{g}_J^0(R)dR, \tag{11}$$

and an element of the matrix $\mathbf{V}_m(R)$ is

$$V_{mnn'}(R) = \langle h_n(\hat{R},\mathbf{Q})|V_m(\mathbf{R},\mathbf{Q})|h_{n'}(\hat{R},\mathbf{Q})\rangle. \tag{12}$$

This formula can be derived by using a matrix Green's function technique; this derivation has been reported in several recent papers[6-10] and will not be repeated here. The formula (10) directly relates the S matrix elements to linear coefficients in the potential providing a close-coupling calculation of $\mathbf{g}_J^0$ has been performed, and the integrals on the right-hand side of Eq. (11) have been calculated.

To show how the linear coefficients $\{c_m\}$ can be related to experimental data, we consider the example of integral cross sections for atom-diatom rotational energy transfer in a body-fixed coordinate system.[11] For other types of scattering properties, collisional systems, or coordinate types, an entirely analogous set of equations are obtained.

The degeneracy-averaged integral cross sections for rotational transitions $j \to j'$ are given by[11]

$$\sigma(j \to j',E) = \frac{\pi}{k_j^2}\sum_{J\Omega\Omega'} \frac{(2J+1)}{(2j+1)}|S_{jj}^{J\Omega'\Omega}(E)|^2, \tag{13}$$

where k_j is the initial wave number and Ω is the body-fixed projection quantum number. Also, $S_{jj}^{J\Omega'\Omega}(E)$ is an S matrix element. Substitution of Eq. (10) into Eq. (13) gives the coupled quadratic equations

$$\sigma_i = \sum_m \sum_n c_m c_n P_{imn} + \sum_m c_m P_{im} + P_i^0, \tag{14}$$

where

$$P_i^0 = \frac{\pi}{k_j^2}\sum_{J\Omega\Omega'} \frac{(2J+1)}{(2j+1)}|S_{jj}^{J\Omega'\Omega 0}(E_i)|^2, \tag{15}$$

$$P_{im} = \frac{\pi i}{k_j^2 2}\sum_{J\Omega\Omega'} \frac{(2J+1)}{(2j+1)}\{[S_{jj}^{J\Omega'\Omega 0}(E_i)]^* U_{jjm}^{J\Omega'\Omega}(E_i)$$

$$- S_{jj}^{J\Omega'\Omega 0}(E_i)[U_{jjm}^{J\Omega'\Omega}(E_i)]^*\}, \tag{16}$$

and

$$P_{imn} = \frac{\pi}{k_j^2 4}\sum_{J\Omega\Omega'} \frac{(2J+1)}{(2j+1)}[U_{jjm}^{J\Omega'\Omega}(E_i)]^* U_{jjn}^{J\Omega'\Omega}(E_i). \tag{17}$$

In Eq. (14), σ_i is an experimental cross section, where i is a collective index for the transition $j \to j'$ and energy E_i. Note that $U_{jjm}^{J\Omega'\Omega}(E_i)$ is a matrix element of $\mathbf{U}_m$ defined in Eq. (11). If rate constants are of interest than it is only necessary to Maxwell–Boltzmann average the P coefficients of Eqs. (15)–(17). Furthermore, for many other scattering properties, such as differential cross sections, an entirely analogous set of coupled quadratic equations to Eq. (14) is obtained.

If a set of suitable experimental cross section data is available (varying in j,j' or E) then Eq. (14) could be used to determine the coefficients $\{c_m\}$ that best fit this data. This inversion procedure will be easiest to carry out when the required coefficients $\{c_m\}$ and $\mathbf{U}_m$ matrix elements are small. Then the quadratic term of Eq. (14), which could cause convergence problems in the fitting procedure, can be neglected. This leaves a set of *linear* simultaneous equations to be solved with real matrix elements, and the best potential coefficients are found from the generalized inverse

$$\mathbf{c} = [\mathbf{P}^T\mathbf{P}]^{-1}\mathbf{P}^T\mathbf{A}, \tag{18}$$

where $\mathbf{c}$ is a column vector with elements c_m and an element of the column vector $\mathbf{A}$ is

$$A_i = \sigma_i - P_i^0. \tag{19}$$

Furthermore, $\mathbf{P}$ has matrix elements P_{im}. Note that if I is the dimension of vector $\mathbf{A}$, and M is the dimension of vector $\mathbf{c}$, then the rank of the matrix $\mathbf{P}$ must equal M and $M \leqslant I$.

When the coefficients $\{c_m\}$ have been obtained using this inversion procedure, a new V_0 potential is constructed by adding

$$\sum_m c_m V_m(R,\mathbf{Q}) \tag{20}$$

to the original $V_0(R,\mathbf{Q})$. A close-coupling calculation is then done with this modified $V_0(R,\mathbf{Q})$ to produce a new $\mathbf{g}_J^0(R)$ and this is used in a new calculation of the $\mathbf{U}_m$ integrals of Eq. (11), where $\mathbf{V}_m$ is left unchanged. A new set of potential coefficients $\{c_m\}$ are then obtained from Eq. (18). This iterative close-coupling procedure is repeated until the coefficients $\{c_m\}$ fall below a given tolerance. The $V_0(R,\mathbf{Q})$ potential will then reproduce the experimental data.

One significant advantage that the above procedure has is that different quantities, such as integral and differential cross sections for several scattering angles and energies, transport properties, and line-broadening parameters, can be fitted simultaneously. Furthermore, other properties such as second virial coefficients could also be included in the fit. We do not claim that the procedure gives a unique inversion of experimental data, but it does provide a practical technique that can be applied to a wide variety of different energy transfer problems and will have its best applications when reasonable guesses at the potential coefficients are already known; for example, these guesses could be obtained from *ab initio* calculations in some cases. The method does require the repeated solution of the close-coupled equations, and this might seem to be an expensive procedure.

However, such computations are now easily feasible when reasonable sizes of basis sets are used and when an efficient close-coupling algorithm is employed for which the integrals of Eq. (11) can be computed inexpensively.

We note that the procedure we have described is similar in spirit to the recent work by Rabitz and co-workers on sensitivity analysis.[12] Their emphasis, however, has been on examining the dependence of scattering properties on parameters such as potential coefficients and not on directly inverting experimental data to obtain the coefficients.

We now describe briefly how the integrals of Eq. (11) can be computed within the framework of the R matrix propagator method.[13] These equations are largely taken from Refs. 10 and 14, but, for completeness, we think it worthwhile collecting together the most relevant formulas here as some minor details differ slightly from that described in Refs. 10 and 14 (see also Refs. 15 and 16).

In the R matrix propagator method, the distance R is divided into small sectors with the ith sector having midpoint R_i and width h_i. The close-coupling matrix with elements (for $J = 0$)

$$k_n^2 \delta_{nn'} - \frac{2\mu}{\hbar^2} V_{0nn'}(R_i) \tag{21}$$

is diagonalized for sector i to yield the eigenvector matrix $\mathbf{T}_i$ with eigenvalues $\{\lambda_{in}^2\}$. The matrix which gives the overlap of the adiabatic eigenvectors with those of the previous sector is

$$\mathbf{Q}_i = [\mathbf{T}_{i-1}]^T \mathbf{T}_i. \tag{22}$$

The scattering solutions for sector i are given by[14]

$$\mathbf{G}_i^0(R) = \mathbf{f}_1^i(R) + \mathbf{f}_2^i(R) \bar{\mathbf{R}}_i, \tag{23}$$

where $\mathbf{f}_1^i$ and $\mathbf{f}_2^i$ are the diagonal matrices with elements

$$f_{1nn}^i(R) = \sin(\lambda_{in}[R - R_i - h_i/2])/\lambda_{in} \tag{24}$$

and

$$f_{2nn}^i(R) = \cos(\lambda_{in}[R - R_i - h_i/2]) \tag{25}$$

for open channels, with sinh and cosh functions for closed channels. We also have

$$\bar{\mathbf{R}}_i = (\mathbf{Q}_i)^T \mathbf{R}_{i-1} \mathbf{Q}_i, \tag{26}$$

where

$$\mathbf{R}_{i-1}$$

is the R matrix for the sector $i - 1$. The R matrix for sector i is then obtained from

$$\mathbf{R}_i = \mathbf{G}_i^0(R_i + h_i/2)\left[\frac{d\mathbf{G}_i^0}{dR}(R_i + h_i/2)\right]^{-1}. \tag{27}$$

In this way, the R matrix can be propagated from sector to sector until the asymptotic region is reached and the global R matrix $\mathbf{R}^G$ is obtained.[13] The S matrix is then obtained from

$$\mathbf{R}^G = (\mathbf{I} - \mathbf{OS}^0)(\mathbf{I}' - \mathbf{O}'\mathbf{S}^0)^{-1}, \tag{28}$$

where $\mathbf{I}$ and $\mathbf{O}$ are the flux normalized incoming and outgoing asymptotic translational solutions.

Just as the R matrix can be propagated from sector to sector, so can the perturbation integrals of Eq. (11) be evaluated numerically by accumulating the contributions to them from each sector.

In sector i, we evaluate the integral

$$\mathbf{X}_{mi} = \frac{2\mu}{\hbar^2} \int_{R_i - h_i/2}^{R_i + h_i/2} dR \, [\mathbf{G}_i^0(R)]^T [\mathbf{T}_i]^T \mathbf{V}_m(R_i)\mathbf{T}_i\mathbf{G}_i^0(R), \tag{29}$$

where the element of the matrix $\mathbf{V}_m(R_i)$ is defined in Eq. (12).

We note here that the $\mathbf{V}_m(R_i)$ matrix has to be evaluated and stored just once in the potential inversion procedure described above since the iteration is being done on the linear coefficients which multiply the $V_m(R)$, not on the $V_m(R)$ themselves. In calculations on polyatomic molecules, this can give significant savings in computer time for iterations after the first, since the evaluation of the integrals of Eq. (12) is not trivial.

The integrals of Eq. (29) are evaluated analytically by substituting Eq. (23) for $\mathbf{G}_i^0(R)$, and by using the simple primitive f_1^i and f_2^i functions of Eqs. (24) and (25). Then, if $\mathbf{B}_{mi}$ is the sum of the contributions from all sectors to the integral (11) up to sector i, we have[10]

$$\mathbf{B}_{mi} = \sum_{j=1}^i \mathbf{X}_{mj} = [\mathbf{Q}_{i+1}]^T \left\{\left[\frac{d\mathbf{G}_i^0}{dR}(R_i + h_i/2)\right]^{-1}\right\}^T$$

$$\times [\mathbf{B}_{mi-1} + \mathbf{X}_{mi}]\left[\frac{d\mathbf{G}_i^0}{dR}(R_i + h_i/2)\right]^{-1} \mathbf{Q}_{i+1}. \tag{30}$$

This is the propagation equation for the integral (11). When the asymptotic region is reached, this integral is transformed[10,15,16] to ensure that $\mathbf{G}_i^0(R)$ has the correct boundary conditions, in accordance with those of Eq. (7), by using the procedure described by Whaley and Light.[10] Thus, if $\mathbf{B}_{mN}$ is the B matrix for the final sector N, the integral (11) for $\mathbf{U}_m$ is

$$\mathbf{U}_m = -4(-1)^J \mathbf{D}^T \mathbf{B}_{mN} \mathbf{D}, \tag{31}$$

where

$$\mathbf{D} = [k^{-1}\cos(kR_N) + \sin(kR_N)\mathbf{R}^G$$

$$+ ik^{-1}\sin(kR_N) - i\cos(kR_N)\mathbf{R}^G]^{-1}k^{-1/2}. \tag{32}$$

Note that the cosine, sine, and $k^{-1/2}$ functions in this formula refer to diagonal matrices, and R_N is the right-hand boundary of the Nth sector.

It is clear from the above equations that the extra work required to calculate the perturbation integrals of Eq. (11) involves a small number of additional matrix multiplications, but no extra matrix inversions, as the matrix inverse in Eq. (30) is required for the R matrix formula (27).

III. INCORPORATON OF THE INVERSION METHOD INTO THE AVCC-IOS TECHNIQUE

We have applied the method, which is described in Sec. II, to the inversion of an experimental vibrational relaxation rate constant[4] for He + CH_3F. We have chosen this problem for several reasons. First, we have recently developed a new quantum method[5] for atom–symmetric top collisions (the AVCC-IOS method) and have computer programs readily available to incorporate the inversion technique into this method. Second, for this type of problem, there is likely to be a wide variety of rate constant data for a range of temperatures, becoming available in the near future.[17] Third, we

have been interested in vibrational relaxation for several years and some approximate information about the potential surfaces for these types of problems has been obtained from *ab initio* calculations (see, for example, Refs. 18–21). This information, however, is far from complete. Fourth, the calculation of vibrational relaxation rate constants is by no means trivial, and the current problem thus presents a very severe test on the computational feasibilty of applying the inversion procedure. We stress that the inversion method might be best applied to areas such as rotationally inelastic differential cross sections where a wealth of very detailed experimental data has recently been published.[2] However, as a first application of the inversion technique, we consider it perfectly reasonable to consider the vibrational relaxation problem for the reasons given above.

The AVCC-IOS method is fully described in Ref. 5, and will not be repeated in detail here. It is a three-dimensional quantum theory that is applicable to the collisions of atoms with symmetric top or near symmetric top molecules. In this section, we describe how the inversion method of Sec. II is incorporated into the AVCC-IOS theory.

A symmetric top has the rotational Hamiltonian

$$\bar{a}\mathbf{j}_x^2 + b\mathbf{j}^2,$$

where $\mathbf{j}^2$ is the total rotational anglar momentum operator of the molecule, and $\mathbf{j}_x$ is the operator corresponding to the projection of $\mathbf{j}$ along the molecule-fixed symmetry axis x. We apply the energy sudden approximation of replacing $\mathbf{j}^2$ by a constant, but we do not approximate $\mathbf{j}_x^2$. This procedure will be most appropriate when b is small but $\bar{a}$ is large. This is the case for CH_3F, as $\bar{a} = 4.27$ cm^{-1} and $b = 0.85$ cm^{-1}. We also apply the centrifugal sudden approximation[11,22] $\mathbf{J}^2 = \hbar^2 J(J + 1)$, where $\mathbf{J}^2$ is the total angular momentum operator of the atom–molecule system. The AVCC-IOS scattering wave function expansion

$$\psi = \sum_{vkt}\psi_v(\mathbf{q})\chi_k^t(\phi)g_{Jvkt}^0(R;\theta) \tag{33}$$

is then applied. Here v is a vibrational quantum number, $\mathbf{q}$ represents the molecular vibrations, ϕ is the variable describing azimuthal molecular rotations, $\chi_k^t(\phi)$ are the azimuthal rotational functions with symmetry index t, and k is the projection quantum number associated with $\mathbf{j}_x$. Furthermore, θ is the spherical polar orientation angle of the atom with respect to the molecule, and is held fixed in the collisional calculations.

With this expansion, the coupled-channel equations are

$$\left[\frac{d^2}{dR^2} + k_{vk}^2 - \frac{J(J+1)}{R^2}\right]g_{Jvkt}^0(R;\theta)$$
$$= \frac{2\mu}{\hbar^2}\sum_{v'k't'}V_{0vkt}^{v'k't'}(R,\theta)g_{Jv'k't'}^0(R;\theta), \tag{34}$$

where

$$k_{vk}^2 = \frac{2\mu}{\hbar^2}[E - E_v - E_k]$$

and

$$V_{0vkt}^{v'k't'}(R,\theta) = \int d\mathbf{q}\int_0^{2\pi}d\phi\,\psi_v(\mathbf{q})\chi_k^t(\phi)$$
$$\times V_0(R,\mathbf{q},\theta,\phi)\psi_{v'}(\mathbf{q})\chi_{k'}^{t'}(\phi). \tag{35}$$

Here, $d\mathbf{q}$ refers to integration over all the normal coordinates and V_0 is the atom–molecule interaction potential defined in Eq. (2). Note that these matrix elements are equivalent to those of Eq. (6). Application of boundary conditions to the coupled-channel equations (34) gives the S matrix element for a $vkt \rightarrow v'k't'$ transition

$$S_{v'k't'vkt}^{J0}(\theta).$$

From this, cross sections for vibrational-rotational transitions in symmetric top molecules are computed. For example, the degeneracy-averaged integral cross section for the $vk \rightarrow v'k'$ transition is given by[5]

$$\sigma(vk \rightarrow v'k') = \frac{1}{(2-\delta_{k0})}\frac{\pi}{2k_{vk}^2}\sum_t\sum_{t'}\sum_{J=0}^{\infty}(2J+1)$$
$$\int_0^{\pi}\sin\theta\,|S_{v'k't'vkt}^{J0}(\theta)|^2d\theta. \tag{36}$$

Rate constants $k(v \rightarrow v')$ for a vibrational transition are then obtained by Maxwell–Boltzmann averaging the $\sigma(vk \rightarrow v'k')$.

In applying the inversion method described in Sec. II to determine the potential parameters $\{c_m\}$ of Eq. (1), we need to compute the Maxwell–Boltzmann average over $\sigma(vk \rightarrow v'k')$ to give the P_i^0 of Eq. (19), and we also require the Maxwell–Boltzmann average over

$$\frac{1}{(2-\delta_{k0})}\frac{\pi i}{4k_{vk}^2}\sum_t\sum_{t'}\sum_{J=0}^{\infty}(2J+1)\int_0^{\pi}\sin\theta\,d\theta$$
$$\times\{[S_{v'k't'vkt}^{J0}(\theta)]^*U_{v'k't'vktm}^J(\theta) \tag{37}$$
$$- S_{v'k't'vkt}^{J0}(\theta)[U_{v'k't'vktm}^J(\theta)]^*\}$$

to give the P_{im} of Eq. (16). Note that the matrix elements in Eq. (37) are

$$U_{v'k't'vktm}^J(\theta)$$
$$= \frac{2\mu}{\hbar^2}\left\{\int_0^{\infty}[g_J^0(R;\theta)]^T V_m(R,\theta)g_J^0(R;\theta)dR\right\}_{v'k't',vkt}, \tag{38}$$

where the V_m matrix is defined in Eq. (12) and is computed simultaneously with the matrix elements of Eq. (35). The inversion equations (18) are then solved to yield the required potential coefficients, with the A vector, in this case, containing the given experimental rate constants.

IV. APPLICATION OF THE INVERSION METHOD TO He + CH₃F

A. Numerical details

The AVCC-IOS method first of all requires the linear coefficients which relate normal coordinates to Cartesian displacements of the atoms in the molecule. To obtain these coefficients, the force field and equilibrium geometry of Overend and Scherer[23] for CH_3F was used in conjunction with the computer program of Gwinn.[24] The vibrations of relevance to room temperature vibrational relaxation are v_3 and v_6, and these were given the experimental frequencies of 1050 and 1200 cm^{-1}, respectively.[23] All calculations reported below refer to ^{4}He collisions, except where stated. Fur-

thermore, all rate constants are calculated for a temperature of 298 K.

The atom–molecule potential V_0, used for the first iteration of the inversion procedure, was given the pairwise exponential form

$$V_0 = \sum_{i=1}^{5} A_i \exp(-B_i R_i),\qquad (39)$$

where the sum is over all the atoms of the molecule and R_i is the distance from atom i of the molecule to the He atom. The He–H and He–C parameters were taken from self-consistent field calculations on He + ethylene.[19] The He–F pair parameters were taken to be equal to the He–C parameters. This is clearly a significant approximation that could be improved upon, but the aim of this work is not to obtain a highly accurate potential for He + CH$_3$F, but rather to demonstrate the convergence and feasibility of the potential inversion method. The parameters used in Eq. (39) are presented in Table I.

The perturbing potential was taken as

$$V = C_6\left(\frac{\tanh[R_C - 3.5]}{R_C^6} + \frac{\tanh[R_F - 3.5]}{R_F^6}\right),\qquad (40)$$

where R_C and R_F are the He–C and He–F distances, respectively, in atomic units. The tanh functions in this formula were used because they damp this long-range potential in the short-range region.[25] We note that long-range terms such as Eq. (40) are very difficult to determine by *ab initio* methods. The aim was to use the inversion method of Sec. II to obtain the C_6 parameter in Eq. (40). To do this, we took the experimental vibrational relaxation rate constant for 298 K as 0.24×10^{-13} cm^3 s^{-1} molecule^{-1} for He + CH$_3$F.[4]

Of course, it would have been possible to have obtained the potential coefficient C_6 by less direct fitting procedures. However, we stress again that the aim here is to present the first application of the inversion method, and it seems sensible to do this initially for a single parameter problem. The power of the technique will eventually lie in the simultaneous determination of many potential parameters. All the equations to do this were discussed in Sec. II, and the application to the many parameter problem will be the subject of future work.

The AVCC-IOS scattering calculations were performed using numerical procedures which are very similar to those presented for He + ethylene collisions.[5] In the case of CH$_3$F, the coupled channel equations divide into four separate types. These are

$$\chi_k^{1v}(\phi) = \cos(k\phi);\quad k = 0,3,6,...,$$
$$\chi_k^{2v}(\phi) = \cos(k\phi);\quad k = 1,2,4,5,...,$$
$$\chi_k^{3v}(\phi) = \sin(k\phi);\quad k = 3,6,9,...,$$
$$\chi_k^{4v}(\phi) = \sin(k\phi);\quad k = 1,2,4,5,...,\qquad (41)$$

where v refers to the vibrational normal mode. For the v_3 mode, which has A symmetry, these four basis function types are not coupled.

To obtain $v_3 = 1 \to 0$ rate constants and perturbation integrals, converged to within 2% for basis type χ_k^{1v}, we required a basis set of 6,6, and 4 azimuthal functions in the $v_3 = 0,1$, and 2 levels. We also needed 11 IOS angles and required six translational energies, which had the values 0.01, 0.03, 0.06, 0.09, 0.17, and 0.24 eV with respect to the $v = 1, k = 0$ level. However, to compare with experiment, it is necessary[4,5] to calculate the Boltzmann average of the $v = 1 \to 0$ rate constants for all four basis sets of Eq. (41), both for the v_3 and v_6 vibrational modes. The rate constants also have to be weighted by a nuclear spin factor, which is 2 for levels of A symmetry (e.g., χ_k^{1v} for v_3) and 1 for those levels with E symmetry (e.g., χ_k^{2v} for v_3). Fortunately, in several test runs with $C_6 = 0.0$, we found that the $v = 1 \to 0$ rate constant was almost the same when $\chi_k^{1v_3}$ was used as when other basis types were used. For example, with $\chi_k^{1v_3}$ alone, the $v = 1 \to 0$ rate constant was 0.68×10^{-14} cm^3 molecule^{-1} s^{-1}, while with both $\chi_k^{3v_3}$ and $\chi_k^{4v_3}$ coupled the result was 0.72×10^{-14} cm^3 molecule^{-1} s^{-1}. Furthermore, when a calculation was done with the coupled basis sets

$$\chi_k^{1v_3}, \chi_k^{2v_3}, \chi_k^{1v_6}, \chi_k^{2v_6},$$

the $v = 1 \to 0$ Boltzmann averaged rate constant was 0.71×10^{-14} cm^3 molecule^{-1} s^{-1}. Thus, it is perfectly reliable to use just basis set $\chi_k^{1v_3}$ in the inversion of the experimental $v = 1 \to 0$ rate constant.

B. Inversion application

The inversion procedure described in Sec. II was incorporated into our AVCC-IOS computer program so that rate constants for general atom–symmetric top collisions could be automatically inverted on the computer. For the He + CH$_3$F problem, we took an initial guess for the C_6 coefficient of Eq. (40) as $-10.00a_0^{-6} E_h$. Table II presents the calculated $v = 1 \to 0$ rate coefficients obtained in each iteration of the inversion procedure. It can be seen that the rate of convergence on the experimental rate coefficient is very good indeed, even though the initial guess for the C_6 coefficient gave a rate constant only half the experimental value. We have also applied the method to a variety of model problems and potentials and find similar promising convergence properties. As a test on the potential we had obtained using the inversion procedure, we also computed the $v = 1 \to 0$ rate constant for ^{3}He + CH$_3$F. This was 0.60×10^{-13} cm^3 molecule^{-1} s^{-1} in the calculations and

TABLE I. Parameters for the potential of Eq. (39).

Interaction	A/E_h	B/a_0^{-1}
He–H	8.00	2.33
He–C	39.92	2.01
He–F	39.92	2.01

TABLE II. Rate constants k ($v = 1 \to 0$) and C_6 coefficients obtained at each iteration in the inversion procedure. The temperature is 298 K.

Iteration	k ($v = 1 \to 0$)/cm^3 s^{-1} molecule^{-1}	$C_6/E_h a_0^{-6}$
0	0.147(− 13)[a]	− 10.00
1	0.227(− 13)	− 14.88
2	0.242(− 13)	− 15.56
3	0.240(− 13)[b]	− 15.44

[a] Numbers in parentheses are powers of 10.
[b] Experimental rate constant used was 0.240×10^{-13} cm^3 molecule^{-1} s^{-1}.

0.58×10^{-13} cm^3 molecule^{-1} s^{-1} in the experiment,[4] which is very good agreement. It would be of interest to use the method to obtain several parameters in a potential simultaneously. This would require, however, very accurate rate constant measurements over a wide range of temperatures. Although such data has not yet been published for vibrational relaxation in He + CH$_3$F, such experiments are currently being done[17] and we hope to use this new data, when it becomes available, to improve the potential we have determined here.

With our new potential for He + CH$_3$F we have predicted the $v = 1 \rightarrow 0$ rate coefficients for temperatures below 298 K. For ^{4}He + CH$_3$F, the predictions are 3.3×10^{-15}, 7.3×10^{-15}, and 1.4×10^{-14} cm^3 s^{-1} molecule^{-1} at 150, 200, and 250 K, respectively. For ^{3}He + CH$_3$F, the calculations give 1.1×10^{-14}, 2.1×10^{-14}, and 3.8×10^{-14} cm^3 s^{-1} molecule^{-1} at 150, 200, and 250 K, respectively.

V. CONCLUSIONS

A method has been described for determining linear parameters in potential energy surfaces from the direct inversion of experimental inelastic scattering data. A scattering perturbation theory approach is used to yield a set of linear equations for determining these parameters. The construction of these equations requires the solution of the close-coupled equations for a given initial guess of the potential energy surface. The iterative procedure is repeated until a self-consistent set of potential parameters are obtained that reproduce the experimental data. The method avoids the use of indirect fitting procedures such as least-squares methods.

The technique has been applied to the inversion of an experimental vibrational relaxation rate constant yielding a C_6 coefficient in a pair potential function for He + CH$_3$F. The azimuthal and vibrational close-coupled, rotational infinite-order sudden method has been adapted for this purpose. The convergence of the inversion technique has been shown to be very promising in these computations.

It is probable that the method will find many applications to the inversion of a variety of inelastic scattering data.

Indeed, the method has the important advantage that it can be used to invert different types of data simultaneously to converge upon the potential parameters.

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