

Infinite order sudden approximation for rotational energy transfer in gaseous mixtures

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Rotational energy transfer in gaseous mixtures has been considered within the framework of the infinite order sudden (IOS) approximation. A new derivation of the IOS from the coupled states Lippmann-Schwinger equation is given. This approach shows the relation between the IOS and CS T matrices and also shows in a rather transparent fashion Secrest's result that the IOS method does not truncate closed channels but rather employs a closure relation to sum over all rotor states. The general CS effective cross section formula for relaxation processes is used, along with the IOS approximation to the CS T matrix, to derive the general IOS effective cross section. It is then observed that this cross section can be factored into a finite sum of "spectroscopic coefficients" $F_n(j'_a j'_b | j_a j_b | L)$ and "dynamical coefficients" $Q_L(k)$. The $F_n(j'_a j'_b | j_a j_b | L)$ can be calculated once and tabulated since they do not depend at all on the particular system considered. The $Q_L(k)$ can be shown to equal the integral inelastic cross section for the transition $j = 0$ to $j = L$, so that if these cross sections are evaluated, either theoretically or experimentally, other types of cross sections can be computed without any further dynamical calculations. In principle, the factorization permits one to calculate other types of cross sections if any one type of cross section has been obtained by some procedure. The functional form can also be used to compact data. This formalism has been applied to calculate pressure broadening for the systems HD-He, HCl-He, CO-He, HCN-He, HCl-Ar, and CO₂-Ar. In order to test the IOS approximation, comparisons have been made to the CS results, which are known to be accurate for all these systems, as well as to several exact close coupling, semiclassical, and experimental values for some of the systems. The IOS approximation is found to be very accurate whenever the rotor spacings are small compared to the kinetic energy, *provided closed channels do not play too great a role*. For the systems CO-He, HCN-He, and CO₂-Ar, these conditions are well satisfied and the IOS is found to yield results accurate to within 10%–15%.

I. INTRODUCTION

A number of gas phase phenomena depend at the microscopic level on the energy and momentum transferred in binary molecular collisions.¹ These have evoked continued experimental and theoretical study because of their technological importance and because of the information they provide about basic intermolecular forces and molecular collision dynamics. Perhaps one of the most extensively studied of the phenomena is the collisional broadening of molecular spectroscopic lines.^{2,3} Unfortunately, application of the theory which relates the various macroscopic phenomena to the intermolecular potential via collision dynamics is computationally formidable, and until recently, nearly all analyses resorted to severe approximations. The last 10 years, however, have seen great strides in the theoretical understanding of molecular collision dynamics.⁴ A cul-

mination of these studies was the application of sophisticated algorithms and powerful digital computers to the brute force numerical solution of the quantum Schrödinger equation for some simple but nontrivial molecular systems. The intermolecular potentials used in these studies were obtained by solving for the electronic energy as a function of nuclear positions, and the close coupling (CC) scattering equations were solved to determine the nuclear motion on these electronic potential energy surfaces. In some of these studies the resulting scattering amplitudes were also used to calculate collision-induced pressure broadening cross sections and other relaxation phenomena.⁵⁻⁹ For those systems where data were available, agreement with experiment was generally very good. Unfortunately, these accurate methods are too expensive to be used routinely. On the other hand, the detailed descriptions they have provided for a few systems have been invaluable for assessing the applicability and accuracy of various approximate methods.

Besides the appearance of a few essentially exact calculations, the last few years have also seen renewed efforts at developing accurate approximate descriptions of molecular collision dynamics. In many cases, these have been applied to pressure broadening and other re-

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laxation phenomena and it has been possible to assess the various approximations by comparison with accurate quantum calculations or with experimental data. These methods have ranged from purely classical descriptions of collision dynamics,¹⁰ through a variety of semiclassical approaches,¹¹⁻¹³ to purely quantal methods. Among the latter are the effective potential (EP) method of Rabitz,¹⁴ the coupled states (CS) approach of McGuire and Kouri¹⁵ and Pack,²⁰ and the decoupled l -dominant approximation (DLD) of DePristo and Alexander.¹⁶ We have recently considered the accuracy of these methods for pressure broadening and other relaxation phenomena.¹⁷⁻¹⁹ For the systems studied, CS was found to be in essentially quantitative agreement with accurate CC quantum values, whereas DLD was somewhat poorer, and EP, while computationally cheaper, was unacceptable for some of the systems.

In the present paper we consider another, even simpler quantum approximation, the infinite order sudden (IOS) method.²⁰ Only collisions of atoms with linear rigid rotors will be discussed explicitly; however, extension to more complex systems is straightforward, and most of our results and conclusions are expected to have general validity. This approximation has been discussed previously by Curtiss,²¹ Pack, and coworkers,²⁰ Secrest,²² and Hunter.²³ It is also related to the "adiabatic" method introduced by Chase²⁴ for nuclear scattering which has been adapted to electron-molecule scattering by Temkin and co-workers²⁵ and to atom-molecule scattering by Thaddeus²⁶ and by Chu and Dalgarno.²⁷ The accuracy of this method for rotational excitation has been considered by comparison with more accurate quantum calculations for a few systems.²⁰

We begin by presenting, in Sec. II A, a new derivation of the IOS method by introducing the energy sudden approximation (i. e., ignoring the energy difference between rotational levels) into the Lippmann-Schwinger formulation of the CS method.²⁸ This derivation serves to emphasize the intimate connection between IOS and CS T -matrices, and we are then able to obtain IOS expressions for pressure broadening and related relaxation phenomena by employing the general CS formulation recently presented by Goldflam and Kouri.²⁹ The present derivation also shows that in computational applications, unlike CC or the decoupling approximations, IOS does *not* truncate the molecular rotational basis set; the energy sudden approximation makes it possible to perform the infinite sum over basis functions by using closure properties. This result has also been obtained by Secrest.²² As will be seen, this is not always a blessing, since the IOS method overestimates the importance of closed channels in certain cases.

Because the CS and IOS methods decouple the effective orbital angular momentum of collision from the molecular angular momentum, it is possible to introduce a generalized partial wave opacity function for phenomenological cross sections. This is done in Sec. II B. These opacities may prove to be computationally convenient since they appear to be smooth functions of the partial

wave, and this will allow for interpolation of computed values.

The IOS approximation leads to great conceptual as well as computational simplifications of collision dynamics. In particular, it effects a separation of the dependence on collision dynamics (i. e., properties of the intermolecular potential) from the dependence on spectroscopic levels (i. e., molecular rotational levels). This separation will allow us in Sec. II C to express various collision cross sections—including integral inelastic cross sections and pressure broadening cross sections—as a sum over a *finite* and, in fact, a small number of dynamical terms multiplied by coefficients which contain all the dependence on molecular rotational levels. From a computational standpoint, this means that one can calculate a relatively small number of quantities in the IOS approximation and these can then be used to generate a wide variety of specific cross sections.

Insofar as the IOS approximation is an accurate description of collision dynamics, the separation into dynamic and spectroscopic factors also has important consequences for the analysis of experimental data. Specifically, it implies that various cross sections are interrelated in the IOS approximation. In principle, then, if the appropriate dynamical factors are obtained from analysis of one type of experiment, say collision-induced pressure broadening, they can be used to predict a different kind of cross section, for example, state-to-state integral inelastic cross sections. As another example, the integral inelastic cross sections between arbitrary states j and j' can all be computed from the inelastic cross sections out of the lowest, $j=0$, level. These ideas are discussed in more detail in Sec. II D.

A sufficient (although perhaps not a necessary) condition for obtaining all of the simplifications discussed above is that the IOS approximation provides a good description of collision dynamics. To examine this point we have performed IOS scattering calculations for a number of atom-linear rigid rotor systems. We have chosen to examine pressure broadening cross sections here because these can be compared readily with other theoretical results. It would, of course, be interesting to consider other types of collisional cross sections as well. In Sec. III A, we discuss details of the computational methods. Pressure broadening cross sections for a number of systems are presented in Sec. III B. Although the IOS approximation is computationally inexpensive compared with, e. g., the CS or EP approximations, it is found to provide predictably good accuracy for many, although not all, of the systems studied here. Because the energy sudden approximation ignores rotational energy spacings, it is not surprising that the method fails unless the kinetic energy of the collision is large compared with the relevant rotational energy spacings. In addition, if the energy is close to threshold so that closed channels play an important role, the IOS approximation breaks down. This is a manifestation of the use of the closure approximation. These conclusions are discussed in greater detail in Sec. III C. Finally, Sec. IV provides a summary and concluding remarks.

II. THEORY

A. Derivation of IOS method

The sudden approximation was first applied to molecular scattering problems by Kramer and Bernstein.³⁰ Later, Curtiss²¹ presented several formal studies of molecular scattering using a rotating frame description and first derived the IOS approximation in the form commonly used today. Next, Pack and co-workers²⁰ studied the IOS method and were the first to carry out detailed computational tests of its accuracy (by comparing results of full close coupling and IOS calculations for Ar + N₂ collisions). Secrest²² derived the IOS method by a technique which is essentially equivalent to that used by Curtiss, although the connection was not recognized until pointed

out by Hunter.²³ The approach involves the use of a continuous transformation to diagonalize the Hamiltonian.

In this section, we present a new derivation of the IOS starting from the McGuire-Kouri form of the coupled states approximation.¹⁵ This will clearly demonstrate the close relationship between CS and the IOS. As a result, we shall view the IOS T -matrix as an approximation to the CS T -matrix. Then all previously derived CS formulas for integral, differential, and relaxation cross sections²⁹ yield the corresponding IOS formulas by simply replacing the CS by the IOS T -matrix.

We begin the derivation of the IOS by considering the CS Lippmann-Schwinger equation (first given by McGuire and Kouri¹⁵ and then rigorously derived by Kouri and Shimoni²⁸) for an atom-linear rigid rotor:

$$\psi(j_0 m_0 | \mathbf{R} \hat{\gamma}) = Y_{j_0 m_0}(\hat{\gamma}) \exp(i \mathbf{k}_{j_0} \cdot \mathbf{R}) - \frac{\mu}{2\pi \hbar^2} \sum_{jm} Y_{jm}(\hat{\gamma}) \int d\mathbf{R}' d\hat{\gamma}' Y_{jm}^*(\hat{\gamma}') \frac{\exp(i k_j |\mathbf{R} - \mathbf{R}'|)}{|\mathbf{R} - \mathbf{R}'|} V(\mathbf{R}', \theta') \psi(j_0 m_0 | \mathbf{R}' \hat{\gamma}'), \quad (1)$$

where μ is the system reduced mass, θ' is the rotor orientation relative to the scattering vector \mathbf{R} , V is the interaction, and $\hbar^2 k_j^2 / 2\mu$ is the relative kinetic energy when the rotor is in the j th state. We now replace k_j in the Green's function by some average wavenumber k , and note that the sums over j, m can then be analytically carried out using the closure relation

$$\sum_{jm} Y_{jm}(\hat{\gamma}) Y_{jm}^*(\hat{\gamma}') = \delta(\hat{\gamma} - \hat{\gamma}'). \quad (2)$$

The integral over $d\hat{\gamma}'$ can be done immediately and the result is then

$$\psi(j_0 m_0 | \mathbf{R} \hat{\gamma}) = Y_{j_0 m_0}(\hat{\gamma}) \exp(i \mathbf{k}_{j_0} \cdot \mathbf{R}) - \frac{\mu}{2\pi \hbar^2} \int d\mathbf{R}' \frac{\exp(i k |\mathbf{R} - \mathbf{R}'|)}{|\mathbf{R} - \mathbf{R}'|} V(\mathbf{R}', \theta) \psi(j_0 m_0 | \mathbf{R}' \hat{\gamma}). \quad (3)$$

We note that the dependence on the initial state enters solely through the inhomogeneity. We can expand the plane wave as

$$\exp(i \mathbf{k}_{j_0} \cdot \mathbf{R}) = \sqrt{4\pi} \sum_l \sqrt{2l+1} i^l Y_{l0}(\hat{\mathbf{R}}) j_l(k_{j_0} R), \quad (4)$$

where we have oriented the space-fixed z axis parallel to \mathbf{k}_{j_0} , and we also expand the Green's function as

$$-\frac{\mu}{2\pi \hbar^2} \frac{\exp(i k |\mathbf{R} - \mathbf{R}'|)}{|\mathbf{R} - \mathbf{R}'|} = -\frac{2\mu k}{\hbar^2} \sum_{lM} Y_{lM}(\hat{\mathbf{R}}) Y_{lM}^*(\hat{\mathbf{R}}') j_l(kR_\zeta) h_l^*(kR_\rho). \quad (5)$$

Then we can define $\psi_{lM}(j_0 m_0 | \mathbf{R} \hat{\gamma})$ by

$$\psi(j_0 m_0 | \mathbf{R} \hat{\gamma}) = \sqrt{4\pi} \sum_{lM} \sqrt{2l+1} i^l Y_{lM}(\hat{\mathbf{R}}) \psi_{lM}(j_0 m_0 | \mathbf{R} \hat{\gamma}). \quad (6)$$

If we substitute Eqs. (4)–(6) into Eq. (3), we obtain

$$\psi_{lM}(j_0 m_0 | \mathbf{R} \hat{\gamma}) = \delta_{M0} j_l(k_{j_0} R) Y_{l0}(\hat{\gamma}) - \frac{2\mu k}{\hbar^2} \int_0^\infty dR' R'^2 j_l(kR_\zeta) h_l^*(kR_\rho) V(\mathbf{R}', \theta) \psi_{lM}(j_0 m_0 | \mathbf{R}' \hat{\gamma}). \quad (7)$$

We then factor out $\delta_{M0} Y_{l0}(\hat{\gamma})$ by writing

$$\psi_{lM}(j_0 m_0 | \mathbf{R} \hat{\gamma}) = \delta_{M0} Y_{l0}(\hat{\gamma}) \psi_{lM}(R, \theta), \quad (8)$$

where $\psi_{lM}(R, \theta)$ satisfies

$$\psi_{lM}(R, \theta) = j_l(k_{j_0} R) - \frac{2\mu k}{\hbar^2} \int_0^\infty dR' R'^2 j_l(kR_\zeta) h_l^*(kR_\rho) V(\mathbf{R}', \theta) \psi_{lM}(R', \theta). \quad (9)$$

Now we note that $\psi_{lM}(R, \theta)$ depends parametrically on the rotor angle θ only through the θ dependence of the potential $V(\mathbf{R}, \theta)$. Other than this, the scattering behaves just like scattering by a spherically symmetric potential since only $M=0$ components of $Y_{lM}(\hat{\mathbf{R}})$ enter and there is no coupling in orbital angular momentum l . It is also noted that in general, $\psi_{lM}(R, \theta)$ depends on the rotor state because of the $k_{j_0} R$ argument of the initial state Bessel function. If k_{j_0} in the inhomogeneity is also approximated by k , then we obtain

$$\psi_i(R, \theta) = j_i(kR) - \frac{2\mu k}{\hbar^2} \int_0^\infty dR' R'^2 j_i(kR') h_i^*(kR') V(R', \theta) \psi_i(R', \theta). \quad (10)$$

Thus, the IOS approximation to the full wavefunction is given by

$$\psi(j_0 m_0 | \hat{\mathbf{R}} \hat{\mathbf{r}}) = Y_{j_0 m_0}(\hat{\mathbf{r}}) \sqrt{4\pi} \sum_l \sqrt{2l+1} i^l Y_{l0}(\hat{\mathbf{R}}) \psi_l(R, \theta). \quad (11)$$

Equations (9)–(11) summarize the IOS approximation for the wavefunction from the point of view of the simplest CS Lippmann–Schwinger equation approach. It is important to note that the IOS wavefunction in the above approximation (i. e., where k_j and k_{j_0} are all replaced by some effective k) factors into two pieces. The first contains all the dynamics while the second has the internal state dependence of the wavefunction. We shall see that such factorizations are a general feature of the IOS approach and have far reaching consequences for all types of cross sections in the IOS approximation. To obtain the IOS approximation to the CS T matrix, we examine the asymptotic form of Eq. (1) to obtain the CS-differential scattering amplitude as

$$f(jm | j_0 m_0 | \hat{\mathbf{R}}) = -\frac{\mu}{2\pi\hbar^2} \int d\mathbf{R}' \hat{\mathbf{r}}' \exp(-ik_j \hat{\mathbf{R}} \cdot \mathbf{R}') Y_{jm}^*(\hat{\mathbf{r}}') V(R', \theta') \psi(j_0 m_0 | \mathbf{R}' \hat{\mathbf{r}}'), \quad (12)$$

and we replace $\psi(j_0 m_0 | \mathbf{R}' \hat{\mathbf{r}}')$ by Eq. (11), the IOS expression. We then expand the plane wave state via

$$\exp(-ik_j \hat{\mathbf{R}} \cdot \mathbf{R}') = 4\pi \sum_{LM} i^{-L} Y_{LM}(\hat{\mathbf{R}}) Y_{LM}^*(\hat{\mathbf{R}}') j_L(k_j R'), \quad (13)$$

and substitute Eqs. (11) and (13) into Eq. (12). After straightforward but tedious manipulation, we obtain³¹

$$f(jm | j_0 m_0 | \hat{\mathbf{R}}) = \frac{i\delta_{mm_0}}{2\sqrt{k_j k}} \sum_l (2l+1) P_l(\hat{\mathbf{z}} \cdot \hat{\mathbf{R}}) \int_{-1}^1 d(\cos\theta) P_{jm}(\cos\theta) T_{lj}(\theta | k) P_{j_0 m}(\cos\theta), \quad (14)$$

where $\hat{\mathbf{z}}$ is the laboratory oriented center of mass z axis, θ is the rotor orientation relative to the scattering vector, and $T_{lj}(\theta | k)$ is the angle dependent or “fixed orientation” IOS T matrix defined by

$$T_{lj}(\theta | k) = \frac{4\mu i}{\hbar^2} \sqrt{k_j k} \int_0^\infty dR R^2 j_l(k_j R) V(R, \theta) \psi_l(R, \theta). \quad (15)$$

With this definition, the “fixed orientation” IOS S -matrix is $[1 - T_{lj}(\theta | k)]$. We can express $S_{lj}(\theta | k)$ in terms of a phase shift $\eta_{lj}(\theta | k)$ according to $\exp[2i\eta_{lj}(\theta | k)]$. We also note that P_{jm} are normalized associated Legendre polynomials. The IOS approximation to the CS T -matrix can be obtained by comparing Eqs. (14) and (15) to the McGuire–Kouri¹⁵ expression for $f(jm | j_0 m_0 | \hat{\mathbf{R}})$, yielding

$$T_{lm}(j | j_0 | k) = \int_{-1}^1 d(\cos\theta) P_{jm}(\cos\theta) T_{lj}(\theta | k) P_{j_0 m}(\cos\theta). \quad (16)$$

In order to completely specify the approximation, we must tell how to choose k and whether k_j in $j_l(k_j R)$ will be approximated. A variety of ways to do this have been suggested. Following Parker and Pack,³¹ in this paper we adopt the simplest choice and set both k and k_j equal to k_{j_0} .

It is important to emphasize that in numerical applications, the IOS approximation, unlike either CC or CS methods, does *not* truncate the internal state expansion of the Green's function. This fact was noted by Secrest²² in deriving the IOS; it is shown quite clearly in the present derivation of the IOS equations using the full space-frame CS Lippmann–Schwinger equation in untruncated form. Instead, the *closure property* is explicitly employed to analytically sum over all (open and closed) rotor states in the Green's function. This is made possible by our having approximated all k_j by k even for the closed channels. The effect is that one has incorrect coupling to closed channels since ordinarily they are damped by a decaying exponential in the Green's function. The result is that we expect the IOS to be inaccurate for transitions which are strongly coupled by the potential to closed channels. Such coupling is most important near threshold and the IOS will fail for such transitions. As the relative kinetic energy increases, such coupling by the potential plays a less important role and the IOS improves.

B. Generalized opacity function

As shown by Goldflam and Kouri,²⁹ the general CS formula for phenomenological relaxation cross sections for linear molecules colliding with atoms is

$$\begin{aligned} \sigma_n(j_a' j_b' | j_a j_b | E) &= \frac{\pi}{k^2} \sum_{m'} (2l+1) \begin{pmatrix} j_a & j_b & n \\ m & -m' & m' - m \end{pmatrix} \begin{pmatrix} j_a' & j_b' & n \\ m & -m' & m' - m \end{pmatrix} \\ &\times (-1)^{j_b + j_b'} \sqrt{\frac{2j_a' + 1}{2j_a + 1}} (\delta_{j_a' j_a} \delta_{j_b' j_b} - \langle j_b' m' | S^l(E_b) | j_b m' \rangle^* \langle j_a' m | S^l(E_a) | j_a m \rangle), \end{aligned} \quad (17)$$

where $\mathbf{S} = \mathbf{I} - \mathbf{T}$, n is the tensor rank of the relaxation mechanism, j_a and j_b are the (spectroscopic) rotational levels, and unprimed and primed j refer to values before and after a collision. The S -matrices are evaluated at total ener-

gies such that the initial relative kinetic energy is the same, i. e.,

$$E = \hbar^2 k^2 / 2\mu = E_a - E(j_a) = E_b - E(j_b), \quad (18)$$

with $E(j)$ the rotational energy of the level j .

The IOS formula is obtained by replacing the CS S -matrices with their IOS approximation

$$\langle j'm | S^I(E_j) | jm \rangle \cong S_{im}(j' | j | k). \quad (19)$$

In this study it will be assumed that the IOS S -matrices are evaluated at the same relative kinetic energy.

It is convenient to introduce the notion of a generalized opacity within the framework of the CS and IOS approximations. To do this, we note that the general phenomenological cross section for the CS approximation [cf. Eq. (17)] can be written in the form

$$\sigma_n(j'_a j'_b | j_a j_b | E) = \frac{\pi}{k^2} \sum_l P_{nl}(j'_a j'_b | j_a j_b | E), \quad (20)$$

where we defined

$$P_{nl}(j'_a j'_b | j_a j_b | E) = \sum_{mm'} \sqrt{\frac{2j'_a + 1}{2j_a + 1}} (-1)^{j_b + j'_b} (2l + 1) \begin{pmatrix} j_a & j_b & n \\ m & -m' & m' - m \end{pmatrix} \\ \times \begin{pmatrix} j'_a & j'_b & n \\ m & -m' & m' - m \end{pmatrix} (\delta_{j_a j'_a} \delta_{j_b j'_b} - \langle j'_b m' | S^I(E_b) | j_b m' \rangle^* \langle j'_a m | S^I(E_a) | j_a m \rangle). \quad (21)$$

The quantity $P_{nl}(j'_a j'_b | j_a j_b | E)$ is a generalized CS opacity in analogy with the opacity function defined for ordinary integral cross sections. The generalized IOS opacity is then obtained by substituting the IOS approximation for the S -matrices. For the systems we have studied, it has been observed that these opacities are smooth functions of the orbital angular momentum quantum number l . This suggests that one can compute the P_{nl} at appropriately chosen values of l and interpolate to obtain the sum.

The notion of a generalized opacity is not as trivial as it might at first appear. To illustrate this point, we note that for pressure broadening of an isolated line Eq. (21) becomes

$$P_{nl}(j_a j_b | j_a j_b | E) = \sum_{mm'} (2l + 1) \begin{pmatrix} j_a & j_b & n \\ m & -m' & m' - m \end{pmatrix}^2 \\ \times (1 - \langle j_b m' | S^I(E_b) | j_b m' \rangle^* \langle j_a m | S^I(E_a) | j_a m \rangle), \quad (22)$$

which contains only *elastic* S -matrix elements. It was therefore expected that this generalized opacity would behave in the same manner as the elastic integral cross section opacity

$$P_l(j - j) = (2l + 1) \sum_m |\langle jm | T^l | jm \rangle|^2, \quad (23)$$

which is usually an oscillatory function of³² l . That the generalized pressure broadening opacity was usually a smooth function was therefore somewhat unexpected. To understand this we note that this generalized cross section is approximately related to *inelastic* integral cross section opacities

$$\text{Re}\{P_{nl}(j_a j_b | j_a j_b | E)\} \cong \frac{1}{2} \left\{ \sum_{j' \neq j_a} P_l(j_a - j') + \sum_{j' \neq j_b} P_l(j_b - j') \right\}, \quad (24)$$

and the latter are generally smooth functions of l .

Finally, we note that the simple form for the generalized opacity function is effected by the decoupling of angular momenta. In the CC method these relaxation cross sections involve products of S -matrices evaluated at different total angular momentum J . Only for integral state-to-state cross sections where $n = 0$ does the double sum over total angular momenta collapse to a single sum. Thus the CS and IOS approximations have the added computational advantage over CC of facilitating interpolation schemes for relaxation cross sections.

C. Factorization of IOS cross sections

In the IOS approximation it is possible to choose k_j and k so that the fixed orientation S -matrix, $S_f(\theta | k)$, is independent of the molecular rotational levels, j and j' . It is also independent of their projection m . This fact allows for great simplification of the IOS formulas. It effects, as shown below, a separation of the various cross sections into dynamical and spectroscopic factors. The dynamical factors contain all the information which varies from system to system, for example, the collisional reduced mass and the shape and strength of the interaction potential. The spectroscopic factors contain all the dependence on the angular momentum of the rotor; they are independent of the specific system and depend only on the usual properties of angular momentum coupling.

To effect this reduction, it is convenient to expand the angle dependence of the IOS fixed-orientation S matrix in

the same set of functions as the ones used to expand the interaction potential. For a linear molecule colliding with an atom these are the Legendre polynomials. Thus,

$$S_l(\theta|k) = \sum_L S_L^l(k) P_L(\cos\theta), \quad (25)$$

where

$$S_L^l(k) = \frac{1}{2}(2L+1) \int_{-1}^1 d(\cos\theta) P_L(\cos\theta) S_l(\theta|k). \quad (26)$$

The above expression indicates the normalization of the Legendre polynomials used here.³³

With this expansion, the integration over rotational functions to obtain S-matrix elements can be done analytically to give

$$S_{lm}(j'|j|k) = \sum_L S_L^l(k) \langle j'm|P_L|jm\rangle \quad (27a)$$

$$= \sum_L S_L^l(k) (-1)^m \sqrt{(2j+1)(2j'+1)} \begin{pmatrix} j & j' & L \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} j & j' & L \\ 0 & 0 & 0 \end{pmatrix}. \quad (27b)$$

Note that the sum on L is finite, restricted by the triangle relations $|j-j'| \leq L \leq j+j'$; also only even values of $j+j'+L$ enter. It is also convenient to express the Kronecker delta function as

$$\delta_{j',j} = \sum_L (-1)^m \sqrt{(2j+1)(2j'+1)} \begin{pmatrix} j & j' & L \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} j & j' & L \\ 0 & 0 & 0 \end{pmatrix} \delta_{L0}. \quad (28)$$

Inserting Eqs. (27) and (28) into the expression for the generalized relaxation cross section then gives

$$\begin{aligned} \sigma_n(j'_a j'_b | j_a j_b | E) &= \frac{\pi}{k^2} \sum_{L, L'} (2L+1) [\delta_{L0} \delta_{L'0} - S_L^l(k) S_{L'}^l(k)^*] \\ &\quad \times \sum_{mm'} (-1)^{j_b + j'_b + m + m'} (2j'_a + 1) \sqrt{(2j_b + 1)(2j'_b + 1)} \begin{pmatrix} j_a & j'_a & L \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \times \begin{pmatrix} j_b & j'_b & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_a & j'_a & L \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} j_b & j'_b & L' \\ m' & -m' & 0 \end{pmatrix} \begin{pmatrix} j_a & j_b & n \\ m & -m' & m' - m \end{pmatrix} \begin{pmatrix} j'_a & j'_b & n \\ m & -m' & m' - m \end{pmatrix}. \end{aligned} \quad (29)$$

The sum over m, m' can be performed using the identity

$$\begin{aligned} \sum_{mm'} (-1)^{j_b + j'_b + m + m'} \begin{pmatrix} j_a & j'_a & L \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} j_b & j'_b & L' \\ m' & -m' & 0 \end{pmatrix} \begin{pmatrix} j_a & j_b & n \\ m & -m' & m' - m \end{pmatrix} \begin{pmatrix} j'_a & j'_b & n \\ m & -m' & m' - m \end{pmatrix} \\ = \frac{(-1)^n}{(2L+1)} \delta_{LL'} \begin{Bmatrix} j_a & j_b & n \\ j'_b & j'_a & L \end{Bmatrix}. \end{aligned} \quad (30)$$

Performing the sum over L' , the cross section Eq. (29) can then be written in the form

$$\sigma_n(j'_a j'_b | j_a j_b | E) = - \sum_L F_n(j'_a j'_b | j_a j_b | L) Q_L(k), \quad (31)$$

where the spectroscopic coefficient is given by

$$\begin{aligned} F_n(j'_a j'_b | j_a j_b | L) &= (-1)^n (2j'_a + 1) \sqrt{(2j'_b + 1)(2j_b + 1)} \\ &\quad \times \begin{pmatrix} j_a & j'_a & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_b & j'_b & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} j_a & j_b & n \\ j'_b & j'_a & L \end{Bmatrix}, \end{aligned} \quad (32)$$

and the dynamical coefficient is given by

$$Q_L(k) = \frac{\pi}{k^2 (2L+1)} \sum_l (2l+1) (|S_L^l(k)|^2 - \delta_{L0}). \quad (33)$$

Before considering the specialization of this formula to specific types of phenomena, several properties of the F_n and Q_L factors are noteworthy. First, we note that the sum over L is limited since the spectroscopic coefficients F_n vanish unless

$$(-1)^{j'_a + j'_a} = (-1)^{j_b + j'_b} = (-1)^L. \quad (34)$$

The F_n vanish unless the L index is within the finite range determined by triangle inequalities. Second, we note that the partial wave sum in Eq. (33) will converge for each value of L . As long as the anisotropy of the interaction potential decreases faster than R^{-2} , for sufficiently large partial waves, $S_l(\theta|k)$ will become independent of the angle θ , and the S_L^l will vanish except for the $L=0$ term; furthermore, because of unitarity, $|S_0^0|$ will then approach unity. Finally, we note that the only complex valued quantities which enter the expression for the generalized cross sections are the S_L^l , and these enter only as $|S_L^l|^2$. Therefore, within the IOS approximation for rigid rotors, all of these generalized relaxation cross sections are real quantities. In particular, this means that IOS predicts *zero pressure-induced line shifts for pure rotational spectra*.

D. Relationships among cross sections

We now will specialize the IOS general relaxation cross section to some specific cases. Because all the system dependent information is contained in a small

number of dynamical Q_L factors, it will follow that the various cross sections are interrelated. Thus, having determined the Q_L from one type of cross section, it is possible to predict other types of cross sections. Also, because the dependence on spectroscopic levels is contained entirely in the F_n coefficients it is possible to make some generalizations about the dependence of cross sections on rotational levels.

The collision-induced broadening of the isolated (i. e., nonoverlapping) spectral lines between rotational levels j_a and j_b is described by the cross section

$$\sigma_n(j_a j_b | j_a j_b | E) = - \sum_L F_n(j_a j_b | j_a j_b | L) Q_L(k), \quad (35)$$

where $n=1$ for dipole spectra and $n=2$ for Raman spectra. It is apparent that only even values of L enter this sum; by the triangle inequalities, L ranges between zero and two times the smaller of j_a , j_b . For the $L=0$ term, which is therefore always included, it is readily shown that

$$F_n(j_a j_b | j_a j_b | 0) \equiv 1. \quad (36)$$

Furthermore, for higher values of L , the spectroscopic coefficient decreases sharply and is only a weak function of j_a and j_b . Thus, for dipole spectra,

$$F_1(j_a j_a + 1 | j_a j_a + 1 | 2) \gtrsim 0.25, \quad (37)$$

$$F_1(j_a j_a + 1 | j_a j_a + 1 | 4) \gtrsim 0.13. \quad (38)$$

Therefore, the pressure broadening cross section is dominated by the $L=0$ term, and is expected to depend only weakly on spectroscopic level. Because Q_L is positive for $L > 0$, the pressure broadening cross section decreases for higher rotational levels. These conclusions are borne out in the computations presented in Sec. III.

Nuclear magnetic resonance spin-lattice relaxation is described by cross sections for spin-rotation ($n=1$) and spin-spin ($n=2$) coupling of the form

$$\sigma_n(j' j' | j j | E) = - \sum_L F_n(j' j' | j j | L) Q_L(k). \quad (39)$$

Except for the tensor rank of the interaction, these are similar to the ordinary integral *inelastic* cross section which can be shown to be given by ($j' \neq j$)

$$\sigma(j \rightarrow j' | E) = - \sigma_0(j' j' | j j | E) = \sum_L F_0(j' j' | j j | L) Q_L(k). \quad (40)$$

We note that for $n=0$, the $L=0$ coefficient is identically zero. It can be shown that the integral *elastic* cross sections cannot be described in an analogous manner; these depend on the dynamics via $\text{Re}(S_L^i)$ as well as $|S_L^i|^2$.

Insofar as the IOS approximation provides a valid description of the collision dynamics, it is seen that the variation of pressure broadening with spectroscopic line contains the same dynamical information as integral inelastic cross sections with *even* Δj . In principle, mea-

surement of the former is sufficient to determine the latter. However, since the variation of linewidth is small compared with the linewidth, it will be difficult to obtain adequate experimental accuracy to do this. In other words, pressure broadening is dominated by the $L=0$ term whereas this term is excluded from inelastic integral cross sections by the triangle inequalities since $j \neq j'$. In this sense, pressure broadening and integral inelastic cross sections will provide complementary information about collision dynamics.

An interesting relationship among different integral inelastic cross sections can be obtained by considering the explicit form of the spectroscopic coefficients,

$$F_0(j' j' | j j | L) = (2j' + 1) \begin{pmatrix} j & j' & L \\ 0 & 0 & 0 \end{pmatrix}^2. \quad (41)$$

Then

$$\sigma(j \rightarrow j' | E) = (2j' + 1) \times \sum_L \begin{pmatrix} j & j' & L \\ 0 & 0 & 0 \end{pmatrix}^2 Q_L(k). \quad (42)$$

Cross sections calculated via Eq. (42) do not satisfy microscopic reversibility, but one can correct for this by setting $k=k_j$ in the π/k^2 factor of the $Q_L(k)$ plus choosing k in the IOS dynamical equations as a symmetric function of j and j' . In cases where the IOS approximation provides an accurate description, the rotational energy differences should be unimportant compared with the kinetic energy. Therefore, one might expect results to be insensitive to specific choices of k .

Finally, the individual $Q_L(k)$ can be shown to be equal to a single integral inelastic cross section by noting that

$$\begin{pmatrix} 0 & j' & L \\ 0 & 0 & 0 \end{pmatrix}^2 (2j' + 1) = \delta_{Lj'}, \quad (43)$$

so that

$$\sigma(0 \rightarrow L | E) = Q_L(k). \quad (44)$$

Then, one can obtain the entire matrix of inelastic cross sections from a knowledge of cross sections for excitation out of the $j=0$ level. Specifically,

$$\sigma(j \rightarrow j' | E + E_j) = (k_0/k_j)^2 (2j' + 1) \times \sum_L \begin{pmatrix} j & j' & L \\ 0 & 0 & 0 \end{pmatrix}^2 \sigma(0 \rightarrow L | E + E_0), \quad (45)$$

where we have explicitly insured microscopic reversibility in the manner suggested above. It is interesting that a similar expression has been obtained previously by Goldflam and Kouri³⁴ from an alternate analysis of atom-molecule collisions. An analogous expression was also obtained by Varshalovich and Khersonsky³⁵ from yet a different analysis.

III. CALCULATIONS

A. Computational methods

The IOS method requires solution of a one-dimensional radial scattering equation, as a function of "fixed" orientation. As usual, the relevant information is contained in the asymptotic behavior which can be described by a

TABLE I. Partial wave cross sections $\sigma_l(0 \rightarrow 2)$ in Å^2 for Ar-N₂ at 300 K.

l	WKB	Exact
1	0.4105-2	0.4183-2
3	0.9331-2	0.9560-2
5	0.1397-1	0.1447-1
7	0.1773-1	0.1865-1
9	0.2034-1	0.2169-1
11	0.2162-1	0.2302-1
13	0.2148-1	0.2228-1
15	0.1999-1	0.2014-1
17	0.1739-1	0.1789-1
19	0.1420-1	0.1553-1
21	0.1128-1	0.1211-1
25	0.1202-1	0.1144-1
30	0.1963	0.1912
37	0.3068	0.2977
44	1.088	1.075
51	2.622	2.601
58	3.796	3.786
65	0.9656	0.9458
72	1.137	1.073
time ^a	~2 min	~20 min

^aCPU time on a Univac 1108 for partial waves 0-80.

phase shift η or an S matrix. These depend on the kinetic energy, partial wave, and orientation and are related by

$$S_l(\theta|k) = \exp[2i\eta_l(\theta|k)]. \quad (46)$$

The S matrix can be obtained by solving the integral equations derived in Sec. II A, e.g., by the numerical method of Sams and Kouri.³⁶ Alternatively, the equivalent differential equation,

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} - \frac{\hbar^2 l(l+1)}{2\mu R^2} + V(R, \theta) - \frac{\hbar^2 k^2}{2\mu} \right] \psi_l(R, \theta) = 0, \quad (47)$$

can be solved, e.g., by numerical integration such as the deVogelaere algorithm³⁷ or by a more sophisticated technique such as the method of Gordon.³⁸

A third possibility is to approximate the phase shift with the WKB expression

$$\eta_l(\theta|k) \cong \int_{r_0}^{\infty} \left\{ \sqrt{k^2 - V(R, \theta) - \left(\frac{l+\frac{1}{2}}{R}\right)^2} - \sqrt{k^2 - \left(\frac{l+\frac{1}{2}}{R}\right)^2} \right\} dR, \quad (48)$$

where r_0 is the classical turning point. The WKB approach is very attractive computationally since the integral can be evaluated efficiently using Pack's²⁰ approach based on Gauss-Mehler quadrature.

In the present study, various results were obtained using the Sams-Kouri method, deVogelaere integration, and/or the WKB approximation. As expected results from the exact integral equation and the exact differential equation agreed to numerical accuracy, four to five significant figures, in systems where both were employed. The WKB approximation was also found to give good accuracy, better than 1% in the final cross sec-

tions, for most systems considered. To demonstrate the accuracy, Table I compares some partial wave opacities computed from the WKB approximation with numerical solution of the integral equations. The WKB method was tested using 10 and 20 Gauss-Mehler points; 10 quadrature points were found sufficiently accurate.

The IOS integral over rotor orientation was done with a standard Gauss-Legendre quadrature. The necessary number of Gauss points can be inferred by noting that an N -point quadrature is exact for polynomials with orders less than $2N+1$. For a given Q_L the integrand is the product of the Legendre polynomial of degree L times the fixed-orientation S matrix. The angle dependence of the S matrix reflects the angle dependence of the potential; a first approximation suggests that the S matrix can be accurately represented by a polynomial of order λ_{max} where λ_{max} is the highest important term in the Legendre expansion of the interaction potential. The highest Q_L which is needed is given generally by $L = 2j_{\text{max}}$ where j_{max} is the highest molecular rotational level of interest. In general then, the number of Gauss points should be chosen such that $N \geq (j_{\text{max}} + \lambda_{\text{max}})$. Table II presents the dependence on number of Gauss points for pressure broadening of HCl by He where the interaction has $\lambda_{\text{max}} = 2$. For broadening of the $(j, j+1)$ line one needs L values to $2j$ and $N \geq j+2$ is seen to give good accuracy as expected.

B. Pressure broadening cross sections

To test the accuracy of the IOS approximation we have computed pressure broadening cross sections for a number of molecules perturbed by atoms: HD-He, HCl-He, CO-He, HCN-He, HCl-Ar, and CO₂-Ar. These were chosen mainly because of the availability of other theoretical values against which the IOS results could be compared. The first four of these systems have been studied within the accurate CC formalism; we have also previously used these four systems to test the CS, DLD, and EP decoupling approximations.¹⁹ The last two systems have been treated previously semiclassically^{12,13}; for these we have now performed CS calculations as well to provide further comparisons. As shown in Sec. II A, IOS is an approximation to the CS approximation, so it is particularly instructive to compare results obtained by these two methods. Furthermore, in the first four sys-

 TABLE II. Convergence of IOS pressure broadening cross sections with number of Gauss-Legendre points for He + HCl. ^a

Line	No. points					
	4	5	6	8	10	12
0-1	7.9148	7.9157	7.9156	7.9156	7.9156	7.1956
1-2	7.7234	7.7234	7.7233	7.7233	7.7233	7.7233
2-3	7.6960	7.6951	7.6951	7.6951	7.6951	7.6951
3-4	7.6296	7.6852	7.6857	7.6857	7.6857	7.6857
4-5	6.1697	7.6406	7.6812	7.6815	7.6815	7.6815
5-6	5.2713	6.5414	7.6487	7.6792	7.6792	7.6792
6-7	4.8646	5.8347	6.7826	7.6777	7.6779	7.6779
7-8	4.6217	5.4967	6.2075	7.6575	7.6770	7.6770

^a $E = 300 \text{ cm}^{-1}$. Loaded sphere potential (see Ref. 10). Results include partial waves $l \leq 25$. Cross sections are in Å^2 .

TABLE III. He-HD pressure broadening cross sections (\AA^2) computed with various scattering approximations.^a

Line	Energy (cm^{-1})	Scattering approximations				
		CC	CS	IOS	DLD	EP
0-1	60	0.8	0.8	4.0	...	1.8
	100	1.2	1.2	5.5	...	2.2
	200	2.3	2.4	8.3	1.4	3.5
	400	4.5	4.5	11.3	3.0	6.0
1-2	60	1.4	1.4	3.8	...	2.7
	100	1.6	1.6	5.3	...	3.0
	200	2.2	2.2	8.0	1.4	4.0
	400	3.9	4.0	10.9	2.5	6.2

^aSee Ref. 6 for the potential employed.

tems CS has been found to be in quantitative agreement with accurate CC values; it is expected to be comparably good in the last two systems as well, so that CS values should provide an accurate standard for comparison.

These systems sample a range of collision parameters. For example, the rotational constant decreases by two orders of magnitude along the sequence HD, HCl, CO, HCN, and CO_2 . Paralleling this decrease in rotational constant is an increase in the anisotropy of the interaction potential. Both of these trends lead to an increase in inelastic cross sections. For the Ar perturbers, the deeper van der Waals well also leads to larger inelasticity. Being heavier, the Ar projectile also samples much higher partial waves than are needed to describe collisions with He. For both Ar and He, however, the important scattering occurs at short range; i. e., none of these systems are dominated by strong long-range interactions which might be expected to be described poorly by the CS and IOS approximations.

1. HD-He. Details of the interaction potential and CC calculation have been reported previously.⁶ Since this system has a rotation constant ($B_e \sim 40 \text{ cm}^{-1}$) large compared with the kinetic energies considered ($E \leq 400 \text{ cm}^{-1}$) IOS is not expected to give an accurate description for the reasons discussed in Sec. II. The results given in Table III bear out these expectations. At the lowest energies considered, IOS gives cross sections a factor of 5 too large; although IOS improves at higher energies, it is still some two to three times too large at the highest energies considered here. As noted before, CS is

TABLE IV. He-HCl pressure broadening cross sections (\AA^2) computed with various scattering approximations.^a

Line	Energy (cm^{-1})	Scattering approximations			
		CC	CS	IOS	EP
0-1	100	5.1	5.1	7.2	4.5
		5.4	5.4	6.8	5.9
		5.1	5.1	7.2	...
0-1	300	8.2	8.2	8.7	7.5
		8.0	8.0	8.4	9.1
		8.1	8.1	8.7	...

^aThe interaction potential was the loaded sphere model of Gordon.¹⁰

TABLE V. He+HCl pressure broadening cross sections (\AA^2) at $E = 480 \text{ K}$.

Line	LS potential ^a		LJ-fit potential ^b	
	CS	IOS	CS	Semiclassical
0-1	8.63	9.09	5.51	6.86
1-2	8.47	8.82	5.45	5.68
2-3	8.50	8.78	5.43	6.04
3-4	8.44	8.77	5.38	6.27
4-5	8.15	8.76	5.27	6.05
5-6	7.60	8.76	5.06	5.58

^aLoaded sphere model potential of Gordon.¹⁰

^bLennard-Jones fit¹³ to the loaded sphere potential.

in excellent agreement with CC for this system, so the error here is due to the energy sudden approximation and not to approximations related to the CS method (i. e., the centrifugal sudden approximation).

2. HCl-He. For this system we have used the loaded sphere model potential of Gordon,¹⁰ who used it to compute pressure broadening cross sections from classical trajectories. This system has also previously been treated within the accurate CC formalism,⁹ the approximate CS formalism,¹⁸ and a semiclassical framework.¹³ Because the rotational constant of HCl ($B_e \sim 10 \text{ cm}^{-1}$) is smaller than that of HD, the IOS method is expected to be generally better for the former than for the latter, and this is confirmed by the results presented in Table IV. As was the case for HD, the IOS method is seen to improve, for a given spectroscopic line, at higher collision energies. It is also seen here that for a given collision energy, IOS is less accurate for higher rotational levels. This can be understood simply in terms of the energy sudden approximation since, for higher rotational levels, the energy spacing between levels increases.

We have also done calculations to compare with the recent semiclassical treatment of this system by Smith *et al.*¹³ These authors use approximations expected to be better for higher rotational levels, and it is of interest to compare IOS values in these higher rotational levels. It appeared initially that the IOS values were some 30%-40% higher than the semiclassical results (see Table V). Since IOS was in better than 10% agreement with CC and CS values for a somewhat lower energy in the previous calculation, we were led to consider possible errors in the semiclassical values. One obvious problem was that the semiclassical calculation was done with a "Lennard-Jones fit" to the loaded sphere potential. First, CS calculations were done for comparison and agreement of these with the IOS values was within 10%-15%, as expected, with the larger differences occurring in higher levels. Second, CS calculations were done with the Lennard-Jones fit used in the semiclassical study. These results demonstrated that these potentials give significantly different results. Table V also compares CS and semiclassical values where both used the LJ-fitted potential. These should provide an indication of the accuracy of the dynamical approximation used by Smith *et al.* It is seen, however, that their procedure of fitting a Lennard-Jones form to the potential can lead to

TABLE VI. He-CO pressure broadening cross sections (\AA^2).^a

Line	Energy (cm^{-1})	CC	CS	IOS	DLD	EP
0-1	60	33	35	37	26	46
	120	28	29	31	26	41
	200	26	26	28	26	37
1-2	60	30	31	34	24	51
	120	26	26	28	23	43
	200	24	24	26	...	38

^aThe interaction potential is the modified *ab initio* (MAI) interaction in Ref. 8.

larger errors than the semiclassical approximation to the dynamics.

3. CO-He. The interaction potential used here was obtained from an *ab initio* calculation and has been used previously in CC calculations for this system⁸; it has also been used to compute pressure broadening within the CS, DLD, and EP approximations.¹⁹ IOS results for this system are presented in Table VI along with the other theoretical values for comparison. The rotation constant for CO ($B_e \approx 1.9 \text{ cm}^{-1}$) is much smaller than the collision energy, so that the IOS approximation is expected to be better here than for HD or HCl. As seen in Table VI, IOS is, in fact, within about 10% of the CC values, with better accuracy at higher collision energies as expected.

We have also performed some calculations for this system to compare with semiclassical results of Smith *et al.*¹³ The semiclassical calculation used a Lennard-Jones fit to the loaded sphere potential of Gordon; we have done IOS calculations using the exact loaded sphere potential. Results are presented in Table VII. The agreement between the IOS and semiclassical result is quite good, but the IOS approximation predicts somewhat weaker line dependence than the semiclassical approximation.

TABLE VII. He-CO pressure broadening cross sections in \AA^2 at $E = 272 \text{ K}$.

Line	Semi-classical ^a	IOS ^b
0-1		25.8
1-2		24.3
2-3	22.3	24.0
3-4	22.0	23.9
4-5	21.9	23.8
5-6	21.7	23.8
6-7	21.6	23.8
7-8	21.5	23.8
8-9	21.3	23.8
9-10	21.0	23.8
10-11	20.9	23.8
11-12	20.7	23.8

^aThe Lennard-Jones fit¹³ to the loaded sphere potential of Gordon¹⁰ was used in these calculations.

^bThe loaded sphere potential¹⁰ was used in these calculations.

TABLE VIII. He-HCN pressure broadening cross sections (\AA^2).^a

Line	Energy (cm^{-1})	CC	CS	IOS	DLD	EP
0-1	120	29	30	31	30	43
	200	28	28	29	29	38
1-2	120	26	26	27	27	38
	200	26	25	26	27	35

^aThe interaction potential is described in Ref. 7.

4. HCN-He. CC calculations on this system have been presented by Green and Thaddeus,⁷ and we have adopted their interaction potential. CS, DLD, and EP calculations have also been reported for this system.¹⁹ IOS values are compared in Table VIII with these previous results. HCN has a rotational constant somewhat smaller than CO, and, as expected, the IOS approximation is quite good for this system.

5. HCl-Ar. Rotational relaxation in this system has been studied in some detail by Neilsen and Gordon¹² within a semiclassical scattering framework. We have adopted the interaction potential labeled "potential 52" by these authors. In addition to the semiclassical pressure broadening cross sections given by Nielsen and Gordon, we have computed coupled states values to compare with the IOS results. These are all given in Table IX. It is seen that the CS and semiclassical results are in good agreement where both are available. Unfortunately, the IOS results are not so good, with the error ranging from 20% to a factor of 2 too high. If accuracy of the IOS approximation were controlled only by the rotational energy spacing relative to the translational energy, one would expect IOS to be as good for this system as it was for HCl-He; since the errors here are much larger, we must look for additional criteria. The main difference is believed to be the stronger inelasticity in this system. Because of the larger anisotropy, larger reduced mass, and deeper van der Waals well, one finds here larger inelastic cross sections and especially a higher probability for multiple quantum transitions. Insofar as accuracy of the IOS method depends on the size of the rotational energy spacing, it must depend on the spacing between strongly coupled levels; the energy spacing between the collisionally coupled levels in HCl-Ar is then much larger than in the weakly inelastic HCl-He. Furthermore, a major failing of the IOS values is

TABLE IX. Ar-HCl pressure broadening cross sections (\AA^2).

Line	$E = 150 \text{ K}$		$E = 398 \text{ K}$			
	IOS	SC ^a	CS	IOS	SC ^a	CS
0-1	126	98	86	101	80	75
1-2	123	85	82	99	57	54
2-3	122	69	65	98	45	46
3-4	122	51	46	97	37	35
4-5	121	37	32	96	31	...

^aSemiclassical values of Neilson and Gordon.¹²

that they do not decrease rapidly with higher spectroscopic level as do the more accurate values. Due to the larger energy spacing at higher rotational levels, the inelasticity drops sharply; this is properly described by accurate dynamical approximations, but not, of course, by the IOS method where *all* rotational energy spacing is ignored. Finally, it should be noted that the relatively deep van der Waals well in this system increases the importance of Feshbach resonances, i. e., the detailed coupling to closed channels, and, as we have discussed in Sec. IIA, this is not properly described by the IOS approximation.

6. $\text{CO}_2\text{-Ar}$. Ar-CO_2 is a very interesting system since many experimental results are available for rotation-vibrational pressure broadening with $j=2-40$. To date, only semiclassical calculations, in which the vibrational effects were neglected, were reported. We performed the IOS calculations of pressure broadening for the $j=2-8$ lines. We also computed the CS pressure broadening cross sections using a limited basis set ($j \leq 18$ states included). These yield reliable cross sections for $j=0-10$. The potential used is a Lennard-Jones fit¹⁵ to the potential surface of Parker, Snow, and Pack.³⁹ The unaveraged results are tabulated in Table X at four energies for the lines $j=2-8$, within the CS and IOS approximations. We note a marked improvement in agreement of the results as the kinetic energy increases. Also, the accuracy of the IOS approximation becomes

TABLE X. Ar-CO_2 pressure broadening cross sections in \AA^2 .^a

Line	Energy (cm^{-1})	CS	IOS
2-3	69.5	130	158.8
	139.0	122	136.6
	347.5	98.0	97.8
	458.5	89.0	89.0
3-4	69.5	121	156.4
	139.0	108	134.4
	347.5	91.0	96.8
	458.5	85.2	88.1
4-5	69.5	109	154.3
	139.0	100	132.9
	347.5	86.5	95.9
	458.5	81.1	87.3
5-6	69.5	107	153.0
	139.0	90.3	131.8
	347.5	80.6	96.1
	458.5	78.5	86.6
6-7	69.5	105	152
	139.0	88.5	131.0
	347.5	78.1	95.5
	458.5	74.0	86.1
7-8	69.5	105	151.3
	139.0	82.8	130.4
	347.5	73.4	95.0
	458.5	72.3	85.6
8-9	69.5	101	105.9
	139.0	78.0	129.7
	347.5	68.6	94.5
	458.5	69.1	85.1

^aThe potential is a Lennard-Jones fit¹⁵ to the *ab initio* potential of Parker *et al.*³⁹

TABLE XI. Ar-CO_2 pressure broadening cross sections in \AA^2 at room temperature.

Line	CS ^a	IOS	Semi-classical ^b	Experiment ^b
2-3	100	96	102	93 ± 14
3-4	101	94	95	90 ± 10
4-5	92	93	91	96 ± 11
5-6	100	93	88	97 ± 12
6-7	96	92	85	107 ± 12
7-8	100	92	83	96 ± 11
8-9	93	91	80	101 ± 11
9-10		91	78	89 ± 8
10-11		91	76	90 ± 8
11-12		90	75	86 ± 7
12-13		90	74	88 ± 12
13-14		90	74	83 ± 10

^aOnly a four point thermal average quadrature was used to obtain the CS result. Thus these results should be expected to be within 10% of the exact quadrature.

^bThese results are taken from the Ref. 13.

worse with higher j . The thermally averaged CS and IOS results are given in Table XI for $T=198$ K and compared with the semiclassical and experimental results. The agreement of CS and IOS with experiment is seen to be generally within uncertainty of the data. Of course, because of the nature of the Lennard-Jones fit to the potential, and the fact that vibrational motion is ignored in the calculations, this is perhaps to be taken with caution. More significant is the generally excellent agreement between the IOS and CS results. The agreement with the semiclassical results is somewhat worse for the higher lines, but still not bad.

C. Discussion

Several conclusions can be drawn from the results presented above. First, it is apparent that accuracy of the IOS approximation varies for the systems studied here. The accuracy appears to be determined mainly by the energy spacings between the relevant rotational levels compared with the collision energy. In order for the energy sudden approximation to be accurate, the rotational spacings must be small compared with the collision energy, and closed channels must be unimportant. Thus, IOS is generally more accurate (for a given collision energy) for systems with smaller rotational constants. This is readily seen along the sequence HD, HCl, CO, and HCN. For the thermal collision energies treated here, IOS is poor for HD with its rotational constant of about 40 cm^{-1} ; it becomes acceptable for HCl with a rotational constant of about 10 cm^{-1} ; it is nearly quantitative for CO and HCN with rotational constants of less than 2 cm^{-1} . For a given spectral line, IOS becomes more accurate at higher collision energies because the rotor spacing becomes smaller compared to the collision energy. Conversely, for a fixed collision energy, IOS becomes less accurate for higher lines, because the rotational energy spacing increases for higher rotational levels.

If the accuracy of IOS depended solely on the ratio of

rotational to collisional energy, we could expect similar accuracy for HCl perturbed by Ar and by He. However, there also appears to be a dependence on the interaction strength since HCl-Ar is not nearly as well treated by IOS as is HCl-He. For the former system, the well depth is significant compared to the collision energy and the closed channel coupling can be very important in such cases. It is then expected that the IOS will fail because the closure approximation does not build in closed channels in the correct way.

For higher rotational levels, IOS pressure broadening cross sections are seen to decrease too slowly with increasing rotational level when compared with CC or CS values. This can be understood as follows. The pressure broadening cross section is given approximately by the sum of inelastic cross sections out of the two spectroscopic levels. In general, inelasticity decreases for higher rotational levels because of the larger energy transfer required for a given Δj transition. This is readily seen for example, in a perturbation treatment where the cross section is related to a matrix element of the interaction potential divided by the energy difference; the coupling matrix elements are roughly independent of rotational level while the energy denominator increases with rotational level. This is the basic reason why pressure broadening cross sections are generally found to decrease for higher spectroscopic levels, and this effect is readily seen, e.g., in CC and CS calculations. In the IOS approximation, however, this effect of rotational energy spacings is ignored, leading to the weak dependence on rotational level observed for IOS pressure broadening cross sections.

We have also performed calculations to compare with the semiclassical approximation recently introduced by Smith *et al.*¹³ These confirm the accuracy of semiclassical dynamics, although, as noted by Smith *et al.*, lower rotational levels are treated less accurately by this technique. Since IOS is most accurate for the lower levels, it might be profitable to employ these methods in conjunction. In this context, however, we note that the Lennard-Jones fit to potentials employed by Smith *et al.* was found to introduce unacceptable errors for some cases. The complementary nature of the semiclassical and IOS approximations may be further illuminated by the following observations. The semiclassical method assumes relative collisional motion on the spherical average of the interaction potential, i.e., the potential is averaged over rotational motion. IOS, on the other hand, treats relative motion at fixed molecular orientations, i.e., the rotational motion is frozen during the collision. The former corresponds to a rotational period short compared to the collision time while the latter corresponds to the opposite extreme. Since the molecule rotates more rapidly in higher rotational levels, it is easy to see that IOS will be more appropriate for lower levels and a semiclassical treatment will be more reasonable in higher levels.

It is also important to note here that the CS approximation has been found to be of quantitative accuracy for all the systems treated here. If one has an accurate potential and wants to predict line shapes accurate to 5% or

better, and if the rotor energy constant is not too small, then the CS method should be used. In addition, the CS approximation can be used as a standard against which other simpler approximations (e.g., the IOS and semiclassical approximations here) can be tested. This point is of great importance, in particular, in cases where the CC calculations are impossible to carry out.

IV. SUMMARY AND CONCLUSIONS

We have given a new derivation of the IOS method which emphasizes that it can be viewed as an approximation to the CS approximation. This serves to emphasize the relationship between the two methods in a direct way. The correct IOS expressions for phenomenological cross sections can then be obtained in a transparent manner from the CS expressions derived previously.¹⁸ A byproduct of this approach is the elucidation of the role of closed channels in the IOS method.

To provide numerical tests of the accuracy of the IOS approximation, we have computed collision-induced pressure broadening cross sections for several systems and compared these with more accurate theoretical values. Accuracy was found to vary widely among the systems considered. Not surprisingly, in view of the energy sudden approximation, IOS was found to be best when the rotational energy spacing between strongly coupled levels was small compared with the translational energy. In all cases, results were found to improve at higher collision energies, and for a fixed collision energy, higher rotational levels were less accurate. Perhaps the most important computational finding was that for "typical" molecules (CO, HCN, CO₂) which have 10–20 or more rotational levels accessible at thermal energies IOS provided quantitative accuracy (better than 10%) for the lower rotational levels; it was only for hydrides (HCl and HD) at thermal energies that results appeared unacceptable.

One of the most significant results of this work is the demonstration that (in this the simplest IOS choice of wavevector independent of rotational level) all the relaxation cross sections, including ordinary integral inelastic cross sections, can be separated into spectroscopic and dynamical factors. The spectroscopic factors are totally independent of parameters specific to the system of interest and can be computed separately once and tabulated. All the system dependent character of the collision can then be expressed in a small number of dynamical factors. Because the various cross sections can be expressed in terms of a few independent dynamical factors, it follows that they are closely interrelated. Thus, if the dynamical factors are obtained from analysis of some experimental or theoretical cross sections, they can be used to predict a variety of other cross sections. As one example, all the integral inelastic cross sections can be expressed in terms of inelastic cross section out of the $j=0$ level. Accuracy of the IOS approximation is a sufficient condition for this factorization to be valid. However, it may prove to be of more general validity; as evidence of this we note that the same interrelationship of inelastic cross sections has been obtained previously^{34,35} from different analyses. We note finally that

a similar factorization can be obtained for differential scattering cross sections and, therefore, for transport phenomena, such as viscosity and diffusion coefficients, as well.

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