Semiclassical theory of the effects of collisions between rotors on molecular spectral line shapes. I

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The semiclassical (WKB) limit of the quantum mechanical expression for the collisional line broadening cross section of the microwave spectrum of gaseous molecules is derived. For the present purpose of considering binary collisions between such species as OCS and CO_2, action-angle-like variables for the classical mechanics of two interacting rotors are developed. Applications can be made to the evaluation of T_2 (microwave line broadening) and T_1 (microwave transient experiments) cross sections and to calculations of rotational and vibrational energy transfer for linear molecule–linear molecule systems.

I. INTRODUCTION

Molecular rotational phenomena have been treated by numerous theoretical approaches.[1] In this paper, equations are presented for a dynamical description of the classical mechanics of two interacting linear rotating molecules. Expressions for T_1 and T_2 cross sections observed in line broadening and microwave transient experiments are then derived. Such theoretical formalism has several applications to recent experimental studies of molecular rotational motion interrupted by collisions.

There is a large body of data concerning collisional line broadening of the microwave spectrum of linear molecules in the gas phase[1a–c] and of microwave transient experiments.[2] A semiclassical method (semiclassical in the sense of Refs. 3 and 4) for microwave line broadening was developed by Fitz and Marcus[5a,b] and extended to microwave transient phenomena by Liu and Marcus.[5c,d] They obtained numerical results for the relevant collisional cross sections by evaluating semiclassical expressions using exact real and (via analytical continuation) complex-valued classical trajectories. The systems considered were limited to those described by the linear rotor–atom model (e.g., OCS–Ar). The expressions developed in the present paper allow this semiclassical treatment of line broadening and microwave transient phenomena to be extended to a much wider variety of systems, including the self-broadening of such molecules as OCS and HCN.[5e]

In considering an entire vibrational–rotational band in the infrared absorption spectrum of CO in a high density of Ar, Koszykowski and Marcus[5f] obtained agreement with experiment using a largely classical treatment for the rotor–atom system. This method could be applied to many more cases via a formalism that includes rotation and vibration of the perturbing molecule.

Recently an exponential model has been proposed for describing molecular rotational energy transfer by Polanyi and co-workers,[6] who have inferred the values of a parameter in their expression from molecular beam measurements. The rotational transition probabilities predicted by this model have been compared with classical trajectory calculations performed by Wong.[7] As in the case of line broadening, these theoretical calculations were performed for a linear rotor–atom model (in this case, HCl–Ar). By means of the present expressions for the dynamics of two rotors, it is possible to extend such calculations[5g] to the recently experimentally studied[6b] system HCl–HX, where X = F, Cl, Br, or I.

Although the rigid rotor approximation has been imposed for the above applications, the formalism permits the direct inclusion of the molecular vibrational motion without difficulty. Thereby, problems involving vibrational energy transfer, which is the subject of extensive experimental study, can be undertaken.[8] One principal problem therein is of computational feasibility because of the large number of vibrational periods which occur during a typical collision.

II. QUANTUM MECHANICAL LINESHAPE

The quantum mechanical line shape expression for the case where the perturber is a linear molecule can be derived by the same methods which have already been applied to systems in which the perturbers have no internal degrees of freedom.[5a–d,5f,9] The line shape expression is given in the present section, and in the next section, its semiclassical limit is obtained. As in earlier work,[5a–d,9] the subscripts i and f refer to values of quantities before and after a spectral transition, respectively, while a primed quantity is understood to be a postcollisional quantity and the absence of a prime implies a precollisional quantity.

The colliding molecules are assumed to be in the gaseous phase and are treated as rigid rotors that undergo binary collisions. As in the previous work,[5a–d,9] only one of the molecules (the "absorber") in each colliding pair is assumed to be capable of interacting with the radiation. Other assumptions; including the impact approximation, have been listed previously.[5a,b,9]

The quantum numbers which are necessary to describe the dynamics of two colliding rigid rotors are, in a total-J basis set, j, j_p, l, h, J, and M, and the translational wave number k. Here j and j_p are the rotational angular momentum quantum numbers of the absorbing and perturbing rotors, respectively; l is the orbital

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angular momentum quantum number for the relative angular motion of the two rotors; h is the angular momentum quantum number resulting from the coupling of j_p and l($h = j_p + l$); J is the total angular momentum quantum number ($J = h + j$); M is the projection of J on a space-fixed z axis; and k is the wave number corresponding to the relative linear momentum of the two rotors.

The ensemble average over perturber properties of the memory function is given by Fano[10]:

$$\{m(\omega)\} = \sum_{\xi\xi'} \rho_\xi \langle\langle \xi' \xi' | m(\omega) | \xi \xi \rangle\rangle \tag{2.1}$$

in Liouville double vector notation[9,11]; ξ and ξ' are pre- and postcollisional states of the perturber. In the present problem, ξ includes the relative velocity of the two rotors, v (via k), and the quantum numbers, j_p, h, l, J, and M. For a rigid rotor, the Boltzmann distribution function ρ_ξ equals $\rho_v \rho_{j_p}$, where ρ_v and ρ_{j_p} are suitably normalized distributions over the states of relative translational velocity and the states of the perturbing molecule's rotation about its own center of mass, respectively.

Ben-Reuven[9b] has given a line shape expression in terms of the T matrices, and has indicated its extension to the cases of perturbers with internal structure. The former expression, Eq. (30) of Ref. 9(b), can be shown to be equivalent to Eqs. (2.3) and (2.4) given by Fitz and Marcus.[5b] With the appropriate inclusion of j_p, the latter expression for the matrix elements of $\{m(\omega)\}$ appearing in the line shape becomes, in the impact approximation (i.e., in the $\omega \to 0$ limit),

$$\langle\langle j_i' j_f', 1, 0 | \{m(\omega)\} | j_i j_f, 1, 0 \rangle\rangle = -i \int_0^\infty 4\pi \rho_v v^3 \sigma_{f'i',fi} dv = -i \langle v \sigma_{f'i',fi} \rangle , \tag{2.2}$$

where 1 and 0 denote the values of the optical transition parameters K ($= j_f - j_i$) and its projection Q on a space-fixed z axis, and where[12]

$$\sigma_{f'i',fi} = \frac{\pi}{k^2} \sum_{\substack{i'i'' \\ j_p' j_p'' J_i' J_f'}} \rho_{j_p} (-1)^{j_i - j_i' + h - h'} (2J_i + 1)(2J_f + 1) \times \begin{Bmatrix} J_f & J_i & K \\ j_i & j_f & h \end{Bmatrix} \begin{Bmatrix} J_f & J_i & K \\ j_i' & j_f' & h' \end{Bmatrix} [\delta_{i'i''} \delta_{f'f} - \langle j_i' j_p' l' h' J_i' | S | j_i j_p l h J_i \rangle \langle j_f' j_p' l' h' J_f' | S | j_f j_p l h J_f \rangle^*] . \tag{2.3}$$

In Eq. (2.3), k equals p_R, the momentum for the relative translational motion of the perturber and absorber, in the units of $\hbar = 1$ used throughout this paper. Any parity quantum numbers needed to describe the states of the absorbing rotor can readily be included at this point. The factor $\delta_{i'i''}$, expressed as $\langle j_i' j_p' l' h' J_i' | j_i j_p l h J_i \rangle$ equals $\delta_{j_i' j_i} \delta_{j_p' j_p} \delta_{l'l} \delta_{h'h}$, and similar remarks apply to $\delta_{f'f}$. Conservation of total angular momentum during the collision requires that $J_i = J_i'$, $J_f = J_f'$, and thus the primes are deleted from these variables.

For the specific case of nonoverlapping lines for a rigid rotor that undergoes the spectral transition $j_i \to j_f$ and undergoes collisions with other rigid rotors, the electric dipole (microwave) absorption spectrum for such a system, in reduced units, has an intensity given by the following expression[5a,b]:

$$I(\omega) = (1/\pi) \mathrm{Im} | \langle j_i | | \mu | | j_f \rangle |^2 \times \left[\frac{\rho_i}{\omega - \omega_0 - d - iw} + \frac{\rho_f}{\omega + \omega_0 + d - iw} \right] . \tag{2.4}$$

In this equation, d and w denote the shift and width, respectively, of the $j_i \to j_f$ line, and ρ_i and ρ_f are normalized Boltzmann factors. Here,

$$w - id = N_p \langle v \sigma_{fi,fi} \rangle , \tag{2.5}$$

where N_p is the number of perturbing rotors per unit volume and the bracket indicates the average over relative velocities shown in the integral in Eq. (2.2). The $\sigma_{fi,fi}$ is given by (2.3).

III. SEMICLASSICAL LIMIT OF THE LINESHAPE

The semiclassical limit of the quantum line shape expression is obtained by introducing semiclassical expressions for the $6-j$ symbols and the S-matrix elements in (2.3), by converting the quantum numbers there to their classical analogs, and by converting the sums to integrals. In units of $\hbar = 1$ which are used throughout this paper, the relationships between classical momenta and quantum numbers are given by[13]

$$\hat{P}_R = k , \quad \hat{j}_i = j_i + \tfrac{1}{2} , \quad \hat{j}_p = j_p + \tfrac{1}{2} , \quad \hat{l} = l + \tfrac{1}{2} , \quad \hat{h} = h + \tfrac{1}{2} , \quad \hat{J}_i = J_i + \tfrac{1}{2} . \tag{3.1}$$

Similar expressions hold for $\hat{j}_f$ and $\hat{J}_f$. For use in expressions soon to be given, one defines two other classical angular momenta $\hat{j} = \frac{1}{2}(\hat{j}_i + \hat{j}_f)$ and $\hat{J} = \frac{1}{2}(\hat{J}_i + \hat{J}_f)$. The momenta $\hat{j}$, $\hat{l}$, $\hat{j}_p$, $\hat{h}$, $\hat{J}$, and $\hat{P}_R$ are the total coupled variables and have conjugate coordinates $\hat{q}_j$, $\hat{q}_l$, $\hat{q}_{j_p}$, $\hat{q}_h$, $\hat{q}_J$, and $\hat{R}$. These coordinates are simply related to a set of $\bar{q}_i$'s by $\bar{q}_i = \hat{q}_i - \hat{R}\omega_i \hat{v}/v^2$, where ω_i is an angular frequency; $\bar{q}_i$ is a constant of the motion, to be evaluated where the interaction potential of the system is negligible; $\hat{v}$ is the relative velocity at $\hat{R}$; and v is the relative velocity at infinite separation, $\hat{R} = \infty$. [For details on the $\bar{q}_i$'s, see Appendix B of Ref. 5(b).] The $\bar{q}_i$'s provide an unambiguous way to compare trajectories independently of the starting and end points of the trajectory, i.e., $\hat{R}$ is sufficiently large that the potential is negligible.

The symmetrized semiclassical expression for the $6-j$ symbol in (2.3) is[5a]

$$\begin{Bmatrix} J_f & J_i & K \\ j_i & j_f & h \end{Bmatrix} = (-1)^{h+j_i+J_f+K} \times [(j_i + j_f + 1)(J_i + J_f + 1)]^{-1/2} d_{0\lambda}^K(\xi) , \tag{3.2}$$

where ξ is the angle between $\hat{J}$ and $\hat{j}$ (vectors whose magnitudes are $\hat{J}$ and $\hat{j}$),[5a] λ is $J_f - J_i$, δ is $j_f - j_i$, and d is a reduced rotational matrix.[14] Analogously defining δ' as $j_f' - j_i'$ and ξ' as the angle between $\hat{J}'$ and $\hat{j}'$, one finds an analogous expression for the second $6-j$ symbol in (2.3), but now with primes on j_i, j_f, h, δ, and ξ.

The first S-matrix element appearing in the line shape expression Eq. (2.3) can be written semiclassically as[3b]

$$\langle j_i' j_\rho' l' h' | S^{J_i} | j_i j_\rho l h \rangle = \sum_{s.p.} \left| \frac{-i\partial(\hat{j}_i', \hat{j}_\rho', \hat{l}', \hat{h}')}{\partial(\overline{w}_{j_i}, \overline{w}_{j_\rho}, \overline{w}_l, \overline{w}_h)} \right|^{-1/2} \exp\left(iF_4(\hat{j}_i \hat{j}_\rho \hat{l}' \hat{h}' \hat{J}_i E_i; \hat{j}_i \hat{j}_\rho \hat{l} \hat{h} \hat{J}_i E_i) + i\frac{\pi}{2}(\hat{l}+\hat{l}') \right), \tag{3.3}$$

where $\overline{w}_i$ equals $\overline{q}_i/2\pi$ and is introduced for notational brevity.[15] F_4 is the generating function[16,17] for transforming from precollisional values of $\hat{j}_i$, $\hat{j}_\rho$, $\hat{l}$, and $\hat{h}$ to postcollisional ones $\hat{j}_i'$, $\hat{j}_\rho'$, $\hat{l}'$, and $\hat{h}'$ and is given by

$$\begin{aligned} F_4 &= F_4(\hat{j}_i' \hat{j}_\rho' \hat{l}' \hat{h}' \hat{J}_i \hat{E}_i'; \hat{j}_i \hat{j}_\rho \hat{l} \hat{h} \hat{J}_i \hat{E}_i) \\ &= -\int_{\hat{l}}^{\hat{l}'} \hat{q}_l d\hat{l} - \int_{\hat{j}_i}^{\hat{j}_i'} \hat{q}_{j_i} d\hat{j}_i - \int_{\hat{h}}^{\hat{h}'} \hat{q}_h d\hat{h} \\ &\quad - \int_{\hat{j}_\rho}^{\hat{j}_\rho'} \hat{q}_{j_\rho} d\hat{j}_\rho - \int_{\hat{P}_R}^{\hat{P}_R'} \hat{R} d\hat{P}_R - \int_{\hat{J}_i}^{\hat{J}_i'} \hat{q}_{J_i} d\hat{J}_i - \hat{l}' \cos^{-1}\hat{P}_R'/[2\mu(E_i' - B\hat{j}_i'^2 - B_\rho \hat{j}_\rho'^2)]^{1/2} + \hat{l} \cos^{-1}\hat{P}_R/[2\mu(E - B\hat{j}_i^2 - B_\rho \hat{j}_\rho^2)]^{1/2}, \end{aligned} \tag{3.4}$$

where R is the distance between the centers of gravity of the two rotors. While $\hat{E}_i' = \hat{E}_i$ and $\hat{J}_i' = \hat{J}_i$, the different symbols are retained to obtain the appropriate derivatives. [The derivatives of (3.4) with respect to $\hat{P}_R$ and $\hat{P}_R'$ are zero, as indeed they must be.] The integration path used in Eq. (3.4) is the classical trajectory that goes from $(\hat{j}_i, \hat{j}_\rho, \hat{l}, \hat{h}, \hat{J}_i, E_i)$ to $(\hat{j}_i', \hat{j}_\rho', \hat{l}', \hat{h}', \hat{J}_i, E_i)$. There are usually several such trajectories, which may be real or complex, and one sums over them, as indicated by the label $\sum_{s.p.}$ in (3.3) (each describes a stationary phase point of an integral expression for S). The F_4 in (3.4) is a generating function which gives barred variables, e.g., $\overline{q}_{j_i}$ and $\overline{q}_{j_i}'$ as $\partial F_4/\partial \hat{j}_i$ and $-\partial F_4/\partial \hat{j}_i'$, respectively.

One does not need the individual S-matrix elements, but rather products as indicated by Eq. (2.3); thus this expression can be simplified. The exponent resulting from the product

$$\langle j_i' j_\rho' l' h' | S^{J_i} | j_i j_\rho l h \rangle \langle j_f' j_\rho' l' h' | S^{J_f} | j_f j_\rho l h \rangle^*$$

is the left hand side of the following expression: The right hand side is obtained by expanding F_4 and F_4^* about a common value, $\hat{j} = \frac{1}{2}(\hat{j}_i + \hat{j}_f)$, etc., and retaining only the leading terms,

$$\begin{aligned} &iF_4(\hat{j}_i' \hat{j}_\rho' \hat{l}' \hat{h}' \hat{J}_i E_i; \hat{j}_i \hat{j}_\rho \hat{l} \hat{h} \hat{J}_i E_i) - iF_4^*(\hat{j}_f' \hat{j}_\rho' \hat{l}' \hat{h}' \hat{J}_f E_f; \hat{j}_f \hat{j}_\rho \hat{l} \hat{h} \hat{J}_f E_f) \\ &= i\frac{\partial F_4}{\partial \hat{j}_i}(j_i - j_f) + i\frac{\partial F_4}{\partial \hat{j}_i'}(j_i' - j_f') + i\frac{\partial F_4}{\partial \hat{J}_i}(J_i - J_f) + i\frac{\partial F_4}{\partial \hat{J}_i'}(J_i' - J_f') + i\frac{\partial F_4}{\partial E_i}(E_i - E_f) + i\frac{\partial F_4}{\partial E_i'}(E_i' - E_f') - 2\Phi, \end{aligned} \tag{3.5}$$

where 2Φ is the imaginary part, if any, of the difference in F_4's. All derivatives and Φ are evaluated at intermediate values of the momenta, e.g., at $\hat{j} = \frac{1}{2}(\hat{j}_f + \hat{j}_i)$; and at values of $\hat{j}'$, $\hat{J}$, and E similarly defined.

Equation (3.5) here is the same as Eq. (3.6) given by Fitz and Marcus,[3b] so their subsequent treatment of the exponential of the products of the S-matrices applies here equally. Thereby, for the present higher dimensional case, one finds that

$$\begin{aligned} &\langle j_i' j_\rho' l' h' | S^{J_i} | j_i j_\rho l h \rangle \langle j_f' j_\rho' l' h' | S^{J_f} | j_f' j_\rho' l' h' \rangle^* \\ &= \left| \partial(\hat{j}', \hat{j}_\rho', \hat{l}', \hat{h}')/\partial(\overline{w}_j, \overline{w}_{j_\rho}, \overline{w}_l, \overline{w}_h) \right|^{-1} e^{i((\theta_1+\theta_2)-2\Phi)}, \end{aligned} \tag{3.6}$$

where

$$\theta_1 + \theta_2 = \overline{q}_j' \delta' - \overline{q}_j \delta + \lambda(q_J' - q_J) + w_E(E_i - E_f) - w_{E'}(E_i' - E_f'). \tag{3.7}$$

In order to yield the cross section $\sigma_{f'i',fi}$ in (2.3), the expressions in Eqs. (3.2) and (3.6) are substituted into Eq. (2.3), and the sums over l, l', h, h', j_ρ, j_ρ' are replaced by integrals. By a change of variable (as in partial averaging)[4j] the Jacobian in (3.3) can be reduced from four dimensions to one, just as in the case of a structureless perturber where the reduction was from two to one[5a-d]:

$$\left| \frac{\partial(\hat{j}', \hat{j}_\rho', \hat{l}', \hat{h}')}{\partial(\overline{w}_j, \overline{w}_{j_\rho}, \overline{w}_l, \overline{w}_h)} \right|^{-1} d\hat{h}' d\hat{l}' d\hat{j}_\rho' = \left| \frac{\partial \hat{J}'}{\partial \overline{w}_j} \right|^{-1} d\overline{w}_h d\overline{w}_l d\overline{w}_{j_\rho}. \tag{3.8}$$

Application of semiclassical theory to the problem of two rotors now involves searching for stationary phase points in one dimension, specifically for the trajectories from the desired $\hat{j}$ to the desired $\hat{j}'$.

In classical mechanics $\hat{j}'$ and the other angular momenta in (3.8) are not restricted to quantized values; hence the latter three are continuous functions of the $\overline{w}_i$. In studying a particular collisional transition $j \to j'$ [$\hat{j}$ is related to j as in Eq. (3.1)], trajectories are computed to determine numerically the functional dependence of $\hat{j}'$ on $\overline{w}_j$, and one evaluates $\partial \hat{j}'/\partial \overline{w}_j$ in Eq. (3.8) as the slope of such a curve at the desired value of $\hat{j}'$ for the given $(\overline{w}_h, \overline{w}_l, \overline{w}_{j_\rho}, \hat{j}, \hat{l}, \hat{j}_\rho, \hat{h}, \hat{J})$. If there are several different values of such $\overline{w}_j$'s that result in that particular value of $\hat{j}'$, the contributions to the S-matrix element are additive as implied by the sum in Eq. (3.3).

By use of Eqs. (3.3) and (3.8), the standard relations for manipulating the $6-j$ symbols,[14] and the symmetrized semiclassical limit of the $6-j$ symbols,[5a] one obtains the semiclassical limit of the relevant cross section $\sigma_{f'i',fi}$ given by Eq. (2.3) as[5a]

$$\sigma_{f'i',fi} = 2\pi \int_0^\infty S(b)\, b\, db, \tag{3.9}$$

where the impact parameter $b = \hat{l}/\hat{P}_R = \hat{l}/\mu v$, and

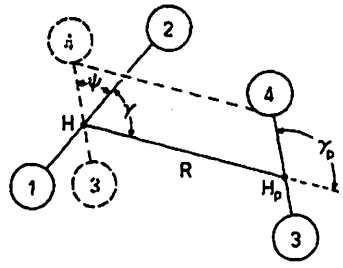

FIG. 1. The angles γ, γ_p and ψ that describe the relative orientation of the two interacting rigid rotors. R denotes the separation between their centers of mass situated at points H and H_p.

$$S(b) = \int_0^\infty d\hat{j}_p \rho_{j_p} \int_{|\hat{j}_p - \hat{l}|}^{\hat{j}_p + \hat{l}} d\hat{h}(\hat{h}/2\hat{l}\hat{j}_p) \times \int_{|\hat{h}-\hat{j}|}^{\hat{h}+\hat{j}} d\hat{J}(\hat{J}/2\hat{j}\hat{h}) \int_0^1 \int_0^1 \int_0^1 d\bar{w}_h d\bar{w}_l d\bar{w}_{j_p} (1 - P') \,. \tag{3.10}$$

Here,

$$P' = \sum_{\delta,\delta'} |\partial \hat{j}'/\partial \bar{w}_j|^{-1} \exp(-2\Phi) D^K_{\delta',\delta}(\alpha\beta\gamma) \tag{3.11}$$

and

$$D^K_{\delta',\delta}(\alpha\beta\gamma) = \sum_{\lambda=-K}^{K} e^{i(\alpha_1+\alpha_2)} d^K_{\delta\lambda}(\xi) d^K_{\delta'\lambda}(\xi') \,. \tag{3.12}$$

The ρ_v in Eq. (2.2) and the ρ_{j_p} above are the standard distribution functions, $(\mu/2\pi kT)^{3/2} \exp(-\mu v^2/2kT)$ and $(2\hat{j}_p B_p/kT) \exp(-\hat{j}_p^2 B_p/kT)$, where B_p is the rotational constant of the perturbing molecule and where μ is the reduced mass of the relative motion. The $\bar{w}$'s denote $\bar{q}/2\pi$'s (as before), and D is a rotation matrix which was shown[5a,b] to describe the effect of a collision in causing phase shifts α and γ in the final and initial planes of rotation, and a reorientation angle β between those two rotational planes.

Each of the other quantities in Eqs. (3.10) and (3.11) has a simple physical interpretation, e.g., $|\partial \hat{j}'/\partial \bar{w}_j|^{-1} \times \exp(-2\Phi)$ is the semiclassical probability that a transition $\hat{j} \to \hat{j}'$ will occur for that particular trajectory, $\hat{h}/2\hat{l}\hat{j}_p$ is $(2h+1)/(2l+1)(2j_p+1)$, i.e., the probability of forming a state of given h for given values of j_p and l. The quantities in Eqs. (3.11) and (3.12) are evaluated for trajectories where $\hat{j}$ has a mean value $(\hat{j}_i + \hat{j}_f)/2$.

For the case of nonoverlapping lines,[5a,b] one needs only the expression where $j_i' = j_i$ and $j_f' = j_f$. For the case of an electric dipole allowed transition, one has $\delta = \delta' = K = K' = 1$ in Eqs. (3.9)–(3.12). The various expressions in the present paper are applied subsequently[5c] to calculate microwave line broadening cross sections.

The actual numerical evaluation of the microwave spectral linewidth in Eq. (2.5) via Eqs. (3.9)–(3.12) requires that the postcollisional values of the total-J coupled action–angle variables $(\hat{q}', \hat{p}')$ be determined from specified precollisional values of these same variables $(\hat{q}, \hat{p})$. This can be achieved by computing exact classical trajectories (i.e., by numerically integrating Hamilton's equations of motion) for those specified precollisional conditions and a specified intermolecular potential function. In principle, Hamilton's equations can be integrated in terms of the $(\hat{q}, \hat{p})$ variables, yet in practice this is sometimes not advisable since computational difficulties arise whenever certain momenta attain values near zero and the conjugate planes of motion concomitantly become undefined.

Such difficulties can be avoided by first transforming the $(\hat{q}, \hat{p})$ to center-of-mass Cartesian coordinates and momenta (ξ, η), as in Ref. 18. Upon numerical integration of Hamilton's equations in terms of these Cartesian variables (ξ, η), as in Appendix A, the postcollisional values of the Cartesian variables (ξ', η') are transformed, again by equations in Ref. 18, to postcollisional total-J coupled action–angle variables $(\hat{q}', \hat{p}')$ for use in evaluating the expressions in Eqs. (3.9)–(3.12).

Further discussion of the computational aspects involved with the use of exact dynamical trajectories in calculating T_2 (linewidth) and T_1 relaxation cross sections, together with numerical results, is given in the next paper of this series.[5c] The sampling method for evaluating these cross sections is described in Ref. 18.

APPENDIX A: INTERMOLECULAR POTENTIAL AND CONSTRAINED EQUATIONS OF MOTION

The relative orientation of the two rotors, and therefore the intermolecular potential for two rigid rotors, is completely specified by the intermolecular separation distance R, the angle γ between the absorber's axis and the line of centers, angle γ_p between the perturber's axis and the line of centers, and angle ψ between the rotor's and perturber's axes, as shown in Fig. 1. To describe the potential itself uniquely, it suffices to specify these variables and to define the angles in the $[0, \pi]$ interval.

One can integrate the equations of motion in action–angle variables, using the relation between γ, γ_p, and ψ and those coordinates, given later in Part II of this series.[5c] If, instead, the trajectories are computed in Cartesian coordinates and momenta (ξ, η) in terms of which the angles γ, γ_p, and ψ are simply expressed, one first transforms the variables $(\hat{q}, \hat{p})$ to the uncoupled variables (q, p) and then to the Cartesian variables (ξ, η) as Eqs. (A14)–(A17) of Ref. 18. The angles that determine the intermolecular potential are easily expressed in terms of the c.m. Cartesian coordinates ξ_i:

$$\psi = \arccos \frac{\xi_1\xi_7 + \xi_2\xi_8 + \xi_3\xi_9}{(\xi_1^2 + \xi_2^2 + \xi_3^2)^{1/2} (\xi_7^2 + \xi_8^2 + \xi_9^2)^{1/2}} \,, \tag{A1}$$

$$\gamma_p = \arccos \frac{\xi_4\xi_7 + \xi_5\xi_8 + \xi_6\xi_9}{(\xi_4^2 + \xi_5^2 + \xi_6^2)^{1/2} (\xi_7^2 + \xi_8^2 + \xi_9^2)^{1/2}} \,, \tag{A2}$$

$$\gamma = \arccos \frac{\xi_1\xi_4 + \xi_2\xi_5 + \xi_3\xi_6}{(\xi_1^2 + \xi_2^2 + \xi_3^2)^{1/2} (\xi_4^2 + \xi_5^2 + \xi_6^2)^{1/2}} \,. \tag{A3}$$

In terms of Cartesian coordinates and momenta (ξ, η) one computes the classical trajectories by numerically integrating Hamilton's equations of motion for the case of a constraint (here, a rigid rotor constraint):

$$\dot{\xi}_i = \eta_i/\mu_i \quad (i = 1 \text{ to } 9) \,, \tag{A4}$$

and

$$\dot{\eta}_i = -\partial V/\partial \xi_i - 2\lambda_i \xi_i \quad (i = 1 \text{ to } 9) \,, \tag{A5}$$

where

$$\lambda_i = (\eta_j^2 + \eta_{j+1}^2 + \eta_{j+2}^2)/(2\tau_i^2\mu_i) \quad (i = 1 \text{ to } 3, 7 \text{ to } 9), \qquad \lambda_i = 0 \quad (i = 4 \text{ to } 6). \tag{A6}$$

For $i = 1, 2, 3$, the absorber indices, $j = 1$, $\mu_i = \mu_a$, and $\tau_i = \tau$ and for $i = 7, 8, 9$, the perturber indices, $j = 7$, $\mu_i = \mu_p$, and $\tau_i = \tau_p$. The orbital motion is not constrained, thus for $i = 4, 5, 6$, $\lambda_i = 0$, $\mu_i = \mu$, and $\tau_i = R$. The λ_1, defined in Eq. (A6) in terms of precollisional dynamical variables, is seen to be the initial rotational kinetic energy of the absorber divided by its moment arm squared and λ_7 is the analogous quantity for the perturber.

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