Rotational spectrum of HD perturbed by He or Ar gases: The effects of rotationally inelastic collisions on the interference between allowed and collisionally induced components

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The spectral line shapes for the HD rotational spectra perturbed by He and Ar gases, which show interference between allowed and collisionally induced dipole transitions, are calculated including the effects of inelastic rotational collisions. The general parametrization of the line shape, including inelastic collisions, requires six independent real parameters as opposed to four in the theory of Herman, Tipping, and Poll [Phys. Rev. A **20**, 2006 (1979)]. Semiclassical calculations based on classical trajectories indicate the importance of the inelastic effects and show qualitative agreement with the experimental parameters. However, it is clear that a full explanation of experimental data will eventually require a full quantum treatment.

I. INTRODUCTION

It is now well known that collision-induced transitions can interfere with allowed transitions to give a line shape that is different from the normal Lorentzian line shape. This interference would, of course, be insignificant if the allowed dipole moment were to dominate. The transitions that are suitable for the study of such interference effects are therefore those with a very small allowed dipole moment. This criterion is met nicely by the rotational spectra of diatomic molecules composed of different isotopes of the same atom. The permanent dipole moments of these molecules arise only from nonadiabatic coupling effects, and are therefore very small. Considerable experimental work has been done with the HD molecule where the interference effects have been observed over a wide range of perturber density and temperature [1–6].

The theoretical understanding of this interference phenomenon was first developed by Herman, Tipping, and Poll [7]. Their theory (referred to hereafter as the HTP theory) explains the main features of the experimental spectrum. Namely, it explains the existence of a dispersion term in the expression for the spectral line shape and accounts for the perturber-density dependence of the integrated absorption. However, detailed comparison with experiment has not been successful [3–5]. It is the hypothesis underlying the work to be reported here that the difficulty lies in the fact that the HTP theory completely ignores m- and J- changing collisions. Both m- and J- changing collisions are known to be crucial in determining the width of molecular rotational spectra [8]. One can expect that they would also play a role in the determination of other collision-related quantities such as the interference parameters. A theory of the interference that includes the role of both m- and J-changing col-

lisions has recently been developed [9]. The exploration of its implications and consequences is the goal of this paper.

The semiclassical calculation of the spectral parameters for both HD-He and HD-Ar systems given here shows much better qualitative agreement with the experiment than that obtained from a HTP-type theory. It also indicates that a complete explanation of HD data will require a full quantum treatment, as to be expected from the large energy spacing of the HD rotational levels and from the comparison of our semiclassical widths with those of a quantal calculation [10]. We have to restrict ourselves to the semiclassical calculation because details of a full quantum calculation of interference parameters are yet to be developed. However, our semiclassical theory should give much better quantitative results for heavier diatomic molecules. Those calculations can be carried out when experimental interest arises, and when data on the collisonally induced dipole of these diatomic molecules, similar to that given by Borysow, Frommhold, and Meyer [11] for HD-He and HD-Ar systems, become available.

The paper is organized as follows. In Sec. II, we give the general parametrization of the line shape including the effects of interference between allowed and collision-induced dipoles. Some general features of this line shape and the effects of inelastic collisions on its parametrization are discussed. We point out that the general parametrization of the spectrum requires six independent real parameters as opposed to four in the HTP theory. Section III gives the theoretical basis for the semiclassical calculation of the line-shape parameters. In Sec. IV, results of such a calculation for the pure rotational spectrum of HD perturbed by He and Ar gases are presented and compared with both the experimental data and the results of an HTP-type calculation. Conclusions are drawn in Sec. V.

II. PARAMETRIZATION OF THE LINE SHAPE

The absorption coefficient $\alpha(\omega)$ derived in Ref. [9] for a transition from the ground state J_g to the excited state J_e can be written in a more transparent form than given in Eq. (67) of Ref. [9], namely,

$$\alpha(\omega) = n_R \left[\frac{4\pi\omega}{3\hbar c} \right] (1 - e^{-\beta\hbar\omega}) P(J_g)$$

$$\times \text{Re}[i(\Delta + i\gamma)^{-1}(\mu_R + n_p\mu_1)(\mu_R + n_p\mu_2)] , \quad (1)$$

where $\beta = 1/k_B T$; ω is the frequency of the incident light; ω_{eg} is the molecular transition frequency; $\Delta = \omega - \omega_{eg}$ is the detuning; and $P(J)$ is the Boltzmann distribution function normalized according to $\sum_J(2J+1)P(J)=1$. It is related to Σ^B used in Ref. [9] by $\Sigma^B_{JJ}=(2J+1)P(J)$. γ is the complex line broadening coefficient given by

$$\gamma = n_p \left[1 - \sum_{\substack{m_e, q, m_g \\ m_e', m_g'}} (-1)^{m_e'+m_e} \begin{bmatrix} J_e & 1 & J_g \\ -m_e' & q & m_g' \end{bmatrix} \begin{bmatrix} J_e & 1 & J_g \\ -m_e & q & m_g \end{bmatrix} \langle J_e m_e' | \hat{S} | J_e m_e \rangle \langle J_g m_g' | \hat{S} | J_g m_g \rangle^* \right]_a , \quad (2)$$

where $\hat{S}$ is the S matrix for the collision between the radiator (HD in this case) and the perturber (He or Ar atom).

$$\mu_R = \langle J_e \| \hat{\mu}_R \| J_g \rangle \quad (3)$$

is the reduced matrix element for the allowed radiator dipole, which can always be taken as real. The number densities n_R and n_p are those of the radiator and perturber, respectively. The dipole moments μ_1 and μ_2 are given in terms of collision-induced dipole operator $\hat{\mu}_e$ by

$$\mu_1 = \sum_{m_e, q, m_g} (-1)^{J_e - m_e} \begin{bmatrix} J_e & 1 & J_g \\ -m_e & q & m_g \end{bmatrix} \int_{-\infty}^{\infty} dt_0 e^{+i\omega_{eg}t_0} [\langle J_e m_e | U^{I\dagger}(t_0, -\infty)[\hat{\mu}_e^I(t_0)]_q U^I(t_0, -\infty) | J_g m_g \rangle^*]_a \quad (4)$$

and

$$\mu_2 = \sum_{J_i} \mu_{2p}(J_i) e^{-\beta(\mathbf{E}_i - \mathbf{E}_g)} , \quad (5)$$

where

$$\mu_{2p}(J_i) = \sum_{m_e, q, m_g, m_i} (-1)^{J_e - m_e} \begin{bmatrix} J_e & 1 & J_g \\ -m_e & q & m_g \end{bmatrix}$$

$$\times \int_{-\infty}^{\infty} dt_0 e^{-i\omega_{eg}t_0} [\langle J_e m_e | U^I(\infty, t_0)[\hat{\mu}_e^I(t_0)]_q U^I(t_0, -\infty) | J_i m_i \rangle \langle J_g m_g | \hat{S} | J_i m_i \rangle^*]_a . \quad (6)$$

$U^I(t, t')$ is the time evolution operator (in the *Hilbert* space) for the radiator-perturber collision (see Sec. III). $\hat{\mu}_e^I(t)$ is the collision-induced dipole operator of the radiator in the interaction picture, i.e.,

$$\hat{\mu}_e^I(t) = e^{iH_R t} \hat{\mu}_e(\mathbf{R}) e^{-iH_R t} , \quad (7)$$

where H_R is the Hamiltonian associated with the internal degrees of freedom of the radiator (HD) and $\mathbf{R}$ is the radial vector connecting the radiator to the perturber.

In Eqs. (2), (4), and (6), the subscript a denotes the average over impact parameter s and velocity v. An angle average has been performed and is represented by the 3-j symbols in Eqs. (2), (4), and (6). Specifically,

$$[\cdots]_a = \int_0^{\infty} dv \, 4\pi v^3 w(v) \int_0^{\infty} ds \, 2\pi s \cdots , \quad (8)$$

where $w(v)$ is the Maxwell-Boltzmann velocity distribution function for the relative motion between the radiator and the perturber. The integration over time of closest approach t_0, as implied in Eq. (67) of Ref. [9], has been written out explicitly in Eqs. (4) and (6).

The dipole moments μ_1 and μ_2, just like γ, are general-ly complex numbers. Defining real parameters $B, S, y_1', y_1'', y_2', y_2''$ according to

$$\gamma = n_p(B + iS) , \quad (9)$$

$$\mu_1 = y_1' + iy_1'' , \quad (10)$$

$$\mu_2 = y_2' + iy_2'' , \quad (11)$$

we obtain the following general parametrization for the absorption coefficient:

$$\alpha(\omega) = n_R \left[\frac{4\pi^2\omega}{3\hbar c} \right] (1 - e^{-\beta\hbar\omega}) P(J_g) |\mu_R|^2$$

$$\times \left[\frac{Bn_p/\pi}{(\Delta - Sn_p)^2 + (Bn_p)^2}(1 + an_p + bn_p^2) \right.$$

$$\left. - \frac{(\Delta - Sn_p)/\pi}{(\Delta - Sn_p)^2 + (Bn_p)^2}(cn_p + dn_p^2) \right] , \quad (12)$$

with real parameters a, b, c, d defined by

$$a = (y_1' + y_2')/\mu_R , \quad (13)$$

$$b = (y_1'y_2' - y_1''y_2'')/\mu_R^2 , \tag{14}$$

$$c = (y_1'' + y_2'')/\mu_R , \tag{15}$$

$$d = (y_1'y_2'' + y_1''y_2')/\mu_R^2 . \tag{16}$$

The line shape is therefore characterized in general by six real parameters (B,S,a,b,c,d), which are independent of the perturber density. B is the usual broadening coefficient (half-width per unit density). S is the frequency shift per unit density. Unlike the usual absorption profiles obtained without the collision-induced dipoles, the profile given by Eq. (12) has a dispersion term whose importance is determined by parameters c and d. Furthermore, the integrated absorption coefficient now depends on the perturber density n_p in contrast to the usual absorption profile. More specifically, we have

$$\int d\omega\, \alpha(\omega)/\omega = \text{const} \times (1 + an_p + bn_p^2) . \tag{17}$$

This equation shows clearly how the parameters a and b can be determined experimentally.

The parametrization given by Eq. (12) is completely general and independent of the semiclassical approximation. Its validity relies only on the binary-collision approximation and the approximation of isolated lines [9]. It applies also to atomic spectra, if a heavy radiator approximation is made [12]. It is obvious from their definitions that the parameters a,b,c,d depend (as do B and S) on both the temperature and on the initial and final states. Such dependence is quite evident in the experimental data on the HD rotational spectrum [5,6]. Our calculations will show that m- and J-mixing is crucial in explaining the dependence of these parameters on the initial and final states.

It can be shown from the unitarity of the U and S matrices that we have the following identity:

$$\mu_1 = \sum_{J_i} \mu_{2p}(J_i) . \tag{18}$$

This means we have only to calculate the $\mu_{2p}(J_i)$ to obtain both μ_1 and μ_2. It is clear from Eqs. (4), (5), and (6) that μ_1 and μ_2 differ from each other in general. The exception occurs either if inelastic collisions are not important, i.e., when

$$\langle J_g m_g | \hat{S} | Jm \rangle \approx 0, \quad J \neq J_g ,$$

or if

$$k_B T \gg \Delta E ,$$

where ΔE is a typical energy spacing. In both of these cases we obtain $\mu_1 = \mu_2$. The number of independent parameters is then only four, and the parametrization given in Eq. (12) becomes equivalent to that of Herman, Tipping, and Poll [7], even though the definitions of the parameters are in fact different in the two treatments [9].

If an effective potential V^{am} is taken that is diagonal in both J and m, i.e.,

$$\langle J'm' | V^{am}(\mathbf{R}(t)) | Jm \rangle = \delta_{J'J}\delta_{m'm} V_J^{am}(\mathbf{R}(t)) , \tag{19}$$

all formulas become much simplified. We have

$$\langle J'm' | U^I(t',t) | Jm \rangle = \delta_{J'J}\delta_{m'm} \exp\left[-i\int_t^{t'} V_J^{am}(t)dt\right] , \tag{20}$$

$$\mu_1 = \mu_2 = \int_{-\infty}^{\infty} dt_0 \mu_a(t_0)$$
$$\times \exp\left[-i\int_{-\infty}^{t_0} [V_{J_e}^{am}(t) - V_{J_g}^{am}(t)]dt\right] , \tag{21}$$

where

$$\mu_a(t_0) = \sum_{m_e,q,m_g} (-1)^{J_e - m_e} \begin{bmatrix} J_e & 1 & J_g \\ -m_e & q & m_g \end{bmatrix}$$
$$\times \langle J_e m_e | [\hat{\mu}_e(t_0)]_q | J_g m_g \rangle . \tag{22}$$

This is our version of the theory of Herman, Tipping, and Poll [7]. Calculations based on this HTP-type theory will be carried out as a benchmark for the full semiclassical calculation, which includes both m and J couplings. The choice for the effective potential V^{am} is discussed in the next section, along with other implications of this HTP approximation.

III. SEMICLASSICAL TREATMENT OF HD–RARE-GAS COLLISIONS

For a linear molecule treated as a rigid rotor, its interaction potential with an atom depends on only two variables R and Θ, where R is the magnitude of $\mathbf{R}$, the radial vector connecting the center of mass of the molecule to the atom; Θ is the angle between $\mathbf{R}$ and the molecular axis. We can always expand this potential as

$$V(R,\Theta) = \sum_{k=0}^{\infty} V^{(k)}(R)P_k(\cos\Theta) . \tag{23}$$

This collisional interaction is treated semiclassically in the same spirit as in, for example, Refs. [8] and [13]. Namely, the spherically symmetric part of the potential $V^{(0)}(R)$, which does not couple different rotational states of the molecule, is used to determine the classical trajectories of the relative motion of the atom and molecule. The time-evolution operator $U^I(t,t')$ is then determined using the anisotropic part of the potential

$$V^a \equiv V - V^{(0)} = \sum_{k=1}^{\infty} V^{(k)}(R)P_k(\cos\Theta) \tag{24}$$

through the equation

$$i\hbar\frac{d}{dt}U^I(t,t') = V^{aI}(\mathbf{R}(t))U^I(t,t') , \tag{25}$$

where

$$V^{aI}(\mathbf{R}(t)) = e^{iH_R t}V^a(\mathbf{R}(t))e^{-iH_R t} \tag{26}$$

and $\mathbf{R}(t)$ is defined by the classical trajectory.

For the HD molecule in its ground electronic state, the rotational wave functions $|Jm\rangle$ are simply the spherical harmonics Y_{Jm}. The matrix elements of V^a between these rotational states are obtained from the spherical-harmonic addition theorem

$$\langle J'm'|V^a(t)|Jm\rangle=(-1)^{m'}[(2J'+1)(2J+1)]^{1/2}$$

$$\times\sum_k\begin{bmatrix}J' & k & J\\-m' & m'-m & m\end{bmatrix}$$

$$\times\begin{bmatrix}J' & k & J\\0 & 0 & 0\end{bmatrix}\left[\frac{4\pi}{2k+1}\right]^{1/2}$$

$$\times Y^*_{km'-m}(\theta(t),\phi)V^{(k)}(R(t))\ .\quad(27)$$

$R(t)$, $\theta(t)$, and ϕ are the coordinates that describe the classical trajectory in a space-fixed frame. Since the trajectories are determined from a spherically symmetric potential, we can always set $\phi=0$ to define the collisional plane. The matrix element of $V^a(t)$ will then always be real.

One usually has available only the potentials for H_2–rare-gas interactions. Such potentials are much simpler than those for HD since the symmetry between Θ and $\pi-\Theta$ restricts the summation in Eq. (23) to even-k terms only. It is straightforward, however, to obtain the HD–rare-gas potentials from those for H_2–rare-gas systems. With nonadiabatic couplings ignored, these two potentials are simply related by a shift of origin from the center of mass of H_2 to the center of mass of HD. It is straightforward to show

$$V^{(k)}_{HD}(R)=\frac{(2k+1)}{2}\int_{-1}^{1}V_{H_2}(R',x')P_k(x)dx\ ,\quad(28)$$

where $P_k(x)$ is the Legendre polynomial and R' and x' are given in terms of R and x by

$$R'=(R^2+\delta^2+2R\,\delta x\,)^{1/2}\ ,\quad(29)$$

$$x'=(Rx+\delta)(R^2+\delta^2+2R\,\delta x\,)^{-1/2}\ ,\quad(30)$$

where $\delta=r_e/6$ with $r_e=0.766\,639\,3$ Å being the average internuclear distance of the H_2 molecule. In Fig. 1 we plot the HD-He potentials $V^{(k)}(R)$ for $k=0,1,2$ calculated from the H_2-He potential of Mulder, Avoird, and Wormer [14]. The less important $k=3$ and $k=4$ components are shown in Fig. 2 along with $V^{(0)}(R)$ for comparison. In all of our calculations, we have found that it is sufficient to include terms only up to $k=3$. Other terms are too small in the classically allowed region to make any significant contributions (see Fig. 2).
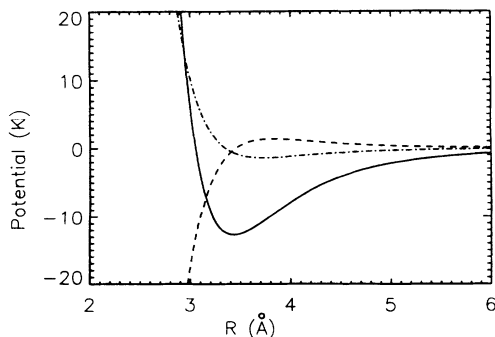

FIG. 1. HD-He potential. Solid line: $V^{(0)}(R)$; dashed line: $V^{(1)}(R)$; dash-dot line: $V^{(2)}(R)$.
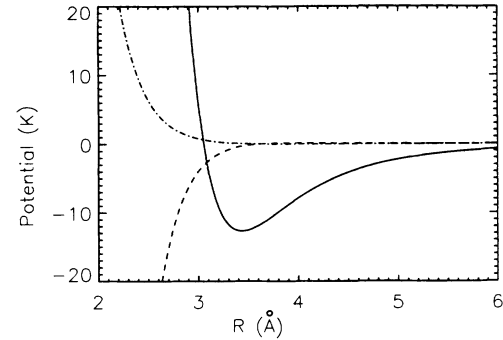

FIG. 2. HD-He potential. Solid line: $V^{(0)}(R)$; dashed line: $V^{(3)}(R)$; dash-dot line: $V^{(4)}(R)$.

Recall that in deriving the expressions for γ,μ_1,μ_2 [9], an angle average has been performed. As a consequence, Eqs. (2), (4), and (6) are invariant under rotation. Specifically, different (space-fixed) quantization axes can be chosen for different impact parameters, with no need of any operations at the end of the calculation to put them all in a single space-fixed frame. We can take the full advantage of this property by choosing the space-fixed z axis, according to which the m state and $\theta(t)$ are defined, to point always to the point of closest approach. We may also take $t=0$ to refer to the point of closest approach. We have then for all impact parameters

$$V^a(-t)=V^a(t)\ .\quad(31)$$

As a consequence we have

$$U^I(-t,-t')=[U^I(t,t')]^*\ .\quad(32)$$

All the information about the collision can now be obtained by integrating the equation

$$i\hbar\frac{d}{dt}U^I(t,0)=V^{aI}(t)U^I(t,0)\ ,\quad(33)$$

from $t=0$ to $t=\infty$ with the initial condition $U(0,0)=I$, which we carry out using the fourth-order Runge-Kutta method [15]. The S matrix is given by

$$\hat{S}=U^I(\infty,0)U^I(0,-\infty)=U^I(\infty,0)[U^I(\infty,0)]^T\ .\quad(34)$$

All the U matrices needed can be constructed from $U^I(\infty,0)$ and $U^I(t,0)$, where $t>0$. For example,

$$U^I(-t,-\infty)=[U^I(t,0)]^*[U^I(\infty,0)]^T\ .\quad(35)$$

The effective potential that we use in the HTP-type theory is taken to be the adiabatic potential averaged over m states

$$V_J^{am}(\mathbf{R})=(2J+1)^{-1}\sum_{m,m',J\neq J}\frac{|\langle Jm|V^a(\mathbf{R})|J'm'\rangle|^2}{E_J-E_{J'}}\ .\quad(36)$$

For a diatomic molecule in a Σ state, the reduced dipole moment of the allowed dipole is given by

$$\langle J'\|\hat{\mu}_R\|J\rangle=(-1)^{J'-J}\!>\sqrt{J_>}D_{vJ',vJ}\ ,\quad(37)$$

where $D_{v'J',vJ}$ is the allowed dipole in the molecular frame and $J_>$ is the greater one of J' and J. For the pure rotational spectrum of HD in its ground electronic and vibrational state, we will take $D_{0J',0J}$ to be independent of J,J' with the value -8.3 D as calculated by Ford and Browne [16]. The minus sign is a result of choosing the

molecular z axis to point from H to D. This convention has to be maintained throughout the calculation.

The induced dipole we use is that of Borysow, Frommhold, and Meyer [11]. For molecule-atom interactions, their more general expression for the induced dipole [see also Ref. (17)] becomes

$$[\hat{\mu}_e(\mathbf{R})]_q = 4\pi \sum_{\Lambda,L} B_\Lambda^{vv'}(L;R) \sum_m (-1)^{1-q} \begin{bmatrix} 1 & \Lambda & L \\ -q & q-m & m \end{bmatrix} Y_{\Lambda q-m}(\Omega) Y_{Lm}(\theta,\phi) ,$$
(38)

where Ω is the orientation of the molecule, and (θ,ϕ) specifies the orientation of $\mathbf{R}$. For HD in its ground vibrational state, $v=v'=0$. The values of $B_\Lambda^{00}(L;R)$ have been given by Borysow, Frommhold, and Meyer [11] in a parametric form as

$$B_\Lambda^{00}(L;R) = A \exp[B(R-R_0)+C(R-R_0)^2]+C_n R^{-n}+C_{n+1}R^{-(n+1)} .$$
(39)

In obtaining Eq. (38) we have also used the fact that due to parity considerations, $\Lambda+L$ must be odd [11,17]. The matrix element of $[\hat{\mu}_e]_q$ between rotational states of HD is then

$$\langle J'm'|[\hat{\mu}_e(\mathbf{R})]_q|Jm\rangle = (-1)^{m'+1-q}[(2J'+1)(2J+1)]^{1/2}$$

$$\times \sum_{\Lambda L}[(2L+1)(2\Lambda+1)]^{1/2}B_\Lambda^{00}(L;R)\begin{bmatrix} J' & \Lambda & J \\ 0 & 0 & 0 \end{bmatrix}\begin{bmatrix} \Lambda & L & 1 \\ m'-m & q+m-m' & -q \end{bmatrix}$$

$$\times \begin{bmatrix} J' & \Lambda & J \\ -m' & m'-m & m \end{bmatrix}\begin{bmatrix} \frac{4\pi}{2L+1} \end{bmatrix}^{1/2} Y_{Lq+m-m'}(\theta,0) ,$$
(40)

in which we have once again taken the collision plane to have $\phi=0$. We note that even though $\hat{\mu}_e$ is itself a dipole (for the combined system of HD plus an atom), it contains many different multipole components related to HD. All these components can contribute to the interference effects (through induced dipole moments μ_1 and μ_2) if J mixing is retained in the collision dynamics. This situation should be compared to an HTP-type theory in which only the $\Lambda=1$ component in Eq. (38) contributes. More specifically, we have then

$$\mu_a(\mathbf{R})=\sqrt{J_e}B_1^{00}(0;R) ,$$
(41)

where μ_a is defined by Eq. (22), and $J_e=J_g+1$. Thus in a HTP-type theory only the $(\Lambda=1, L=0)$ component contributes to the induced dipole moment [Eq. (21)].

Finally, the energy-level constants of HD are taken to be the same as those used by Green in his calculations [10], i.e,

$$E_J=B_0J(J+1)-D_0J^2(J+1)^2 ,$$
(42)

with $B_0=44.6586$ cm^{-1}, and $D_0=0.025\,691$ cm^{-1}.

IV. RESULTS AND DISCUSSIONS

To check the computational procedure, we first calculated the broadening cross sections for the rotational spectrum of HCl perturbed by Ar gas. The results for $E=398$ K are presented in Table I along with those for a similar calculation by Neilsen and Gordon [8]. The highest J state included in our calculation is $J_{max}=7$. The total number of states included is therefore

$(J_{max}+1)^2=64$. The impact parameter is integrated over 21 points from 0 to 8.5 Å. The agreement between the two calculations is excellent.

To check the validity of the semiclassical approximation, we compare in Table II the semiclassical HD-He broadening cross section calculated using the H_2-He potential [MSV(GH)1] of Shafer and Gordon [18] with the full quantum results of Green [10] using the same potential. We see that for small collision energies, the semiclassical calculation gives poor results for the $0\to1$ transition (primarily because of its overestimation of the inelastic rates at these energies). However, the semiclassical result is quite reasonable for the $1\to2$ transition, and the overall agreement with quantum calculation improves as one goes to higher collision energies. We therefore expect our semiclassical calculation to give reasonable results for $1\to2$ and $2\to3$ transitions, especially at high temperatures.

TABLE I. Broadening cross section (Å^2) of HCl perturbed by Ar at $E=398$ K.

Transition	Neilson and Gordon [8]	Present
$R(0)$	79.88	74.71
$R(1)$	57.44	59.56
$R(2)$	45.16	47.97
$R(3)$	37.38	37.14
$R(4)$	30.63	28.59

TABLE II. Broadening cross section ($\mathring{A}^2$) of HD perturbed by He.

Transition	Green [10]	Present
	$E = 100$ cm^{-1}	
$R(0)$	1.15	2.36
$R(1)$	1.60	1.37
	$E = 200$ cm^{-1}	
$R(0)$	2.32	3.81
$R(1)$	2.21	2.76
	$E = 400$ cm^{-1}	
$R(0)$	4.47	5.81
$R(1)$	3.90	4.92
	$E = 600$ cm^{-1}	
$R(0)$	6.06	7.05
$R(1)$	5.42	6.32

TABLE III. Broadening coefficient B (10^{-2}cm^{-1}amagat^{-1}) of HD perturbed by He.

Transition	Experimental [6]	HTP	Semiclassical
	$T = 77$ K		
$R(0)$	0.15	3.7×10^{-2}	0.31
$R(1)$	0.20	4.2×10^{-5}	0.19
$R(2)$	0.12	6.5×10^{-8}	0.09
	$T = 195$ K		
$R(0)$	0.52	0.46	0.93
$R(1)$	0.51	7.4×10^{-4}	0.71
$R(2)$	0.41	1.2×10^{-6}	0.48
	$T = 295$ K		
$R(0)$		1.2	1.4
$R(1)$	1.1	2.7×10^{-3}	1.2
$R(2)$	0.68	4.3×10^{-6}	0.90

TABLE IV. Broadening coefficient B (10^{-2}cm^{-1}amagat^{-1}) of HD perturbed by Ar.

Transition	Experimental [6]	HTP	Semiclassical
	$T = 77$ K		
$R(0)$		0.22	1.3
$R(1)$		1.2×10^{-4}	0.72
$R(2)$		1.8×10^{-7}	0.29
	$T = 195$ K		
$R(0)$	1.4	1.3	2.2
$R(1)$	1.0	1.3×10^{-3}	1.6
$R(2)$	0.86	2.0×10^{-6}	0.96
	$T = 295$ K		
$R(0)$		2.5	2.9
$R(1)$	1.5	4.4×10^{-3}	2.3
$R(2)$	1.1	6.8×10^{-6}	1.6

TABLE V. Interference parameter a (10^{-3} amagat^{-1}) of HD perturbed by He.

Transition	Experimental [6]	HTP	Semiclassical
	$T = 77$ K		
$R(0)$	6.0(16)	4.33	2.99
$R(1)$	6.2(7)	4.34	4.26
$R(2)$	4.4(15)	4.34	6.47
	$T = 195$ K		
$R(0)$	$-11.4(38)$	5.84	2.97
$R(1)$	$-0.4(9)$	6.06	4.83
$R(2)$	2.34(92)	6.06	6.45
	$T = 295$ K		
$R(0)$		6.58	2.82
$R(1)$	5.7(9)	7.22	4.91
$R(2)$	3.9(8)	7.22	6.86

Table III gives the broadening coefficients of HD perturbed by He gas at $T = 77$ K, $T = 195$ K, and $T = 295$ K. Results of both a semiclassical and a HTP-type calculation using the potential of Mulder, Avoird, and Wormer [14] are compared with the experimental data [6]. Similar results for the broadening coefficients of HD perturbed by Ar gas are presented in Table IV. Here the HD-Ar potential of LeRoy and Hutson [19] is used (the potential for $v = 0, j = 1$ in their Table X). For each temperature, the velocity average is carried out by a four-point Gaussian-type quadrature [20]. For each velocity, 21 impact parameters are integrated over for HD-He and 31 for HD-Ar. In the semiclassical calculation, all states up to $J = 4$ are included. These parameters are chosen so that all of the results converge well. Clearly the semiclassical results for both HD-He and HD-Ar systems show good agreement with the experiment except for $R(0)$ transitions. The HTP-type calculation fails completely in giving the correct broadening coefficients for both the $R(1)$ and $R(2)$ transitions: an indication of the importance of m-and J-mixing effects. It gives reasonable results, in fact better than the semiclassical calculation, for

TABLE VI. Interference parameter a (10^{-3} amagat^{-1}) of HD perturbed by Ar.

Transition	Experimental [6]	HTP	Semiclassical
	$T = 77$ K		
$R(0)$		6.20	2.03
$R(1)$		6.28	5.43
$R(2)$		6.28	15.8
	$T = 195$ K		
$R(0)$	1.08(97)	7.18	2.20
$R(1)$	$-3.93(72)$	7.84	4.03
$R(2)$	9.5(67)	7.84	8.40
	$T = 295$ K		
$R(0)$		7.48	2.46
$R(1)$	1.8(3)	8.92	3.22
$R(2)$	6.1(2)	8.92	7.80

TABLE VII. HTP and semiclassical results for the interference parameters c (amagat^{-1}) at $T=195$ K.

Transition	HD perturbed by He		HD perturbed by Ar	
	HTP	Semiclassical	HTP	Semiclassical
$R(0)$	-6.7×10^{-4}	-1.5×10^{-3}	-1.4×10^{-3}	1.1×10^{-3}
$R(1)$	-2.6×10^{-5}	-1.3×10^{-3}	-4.4×10^{-5}	-2.1×10^{-4}
$R(2)$	-1.0×10^{-6}	-3.1×10^{-4}	-1.7×10^{-6}	1.3×10^{-3}

$R(0)$ transitions only because the ground $J=0$ state has no m degeneracy. This helps to confirm our earlier assessment that the semiclassical calculation can overestimate the inelastic rates.

Results for the interference parameter a for HD-He and HD-Ar systems are presented in Table V and Table VI, respectively. The HTP results agree with calculations based on the original HTP theory [5,6]. It should be observed, however, that at a fixed temperature, the HTP-type calculation give virtually identical results for all transitions except $R(0)$. This is a consequence of $U^I\approx1$ for these transitions. The experimental data [6], on the other hand, are strongly transition dependent. This dependence shows up clearly in the semiclassical calculations. For example, for the HD-Ar system at 295 K, the experimental parameter a changes from 1.8×10^{-3} amagat^{-1} for $R(1)$ to 6.1×10^{-3} amagat^{-1} for $R(2)$, and the semiclassical result changes from 3.22×10^{-3} amagat^{-1} to 7.8×10^{-3} amagat^{-1}. However, it cannot be said that there is any truly quantitative agreement between theory and experiment for the interference parameters. The calculations that use our stated potentials do not give negative a, which are observed for some transitions. Such destructive interference is indeed allowed in our theoretical framework. By making suitable adjustments to the potentials it is straightforward to obtain negative a values. For our present calculations, however, negative a can be obtained only if we make significant changes to the potential.

A curious fact here is that our broadening coefficients for HD-He agree better with experiment than those for HD-Ar. Yet the opposite seems to be true for the interference parameter a. Is this an indication that the induced dipole moment we used for HD-Ar [11] is more accurate than that for HD-He [11]? Or should we attribute all disagreements to quantum-mechanical effects? In this regard we note that the a parameter is quite sensitive to the region around the turning point of the trajectory (the point of closest approach) where the induced dipole is greatest. This is precisely the region where a classical description is the least valid. We hope to be able to answer some of these questions in the future.

As mentioned earlier, in the HTP theory $U^I\approx1$ for all transitions except $R(0)$, and as a consequence the interference parameter a is basically the same for all these transitions. Another consequence is that the induced dipole moment [Eq. (21)] is almost real for these transitions, giving rise to very small asymmetry parameters c and d (compared to a and b, respectively). Table VII compares the HTP and semiclassical results for the asymmetry parameter c at $T=195$ K, which shows that for transitions $R(1)$ and $R(2)$ the HTP results are orders of magnitude smaller than the semiclassical results. Even though it is somewhat premature at this point to compare these results with experimental data that need to be reanalyzed within the present theoretical framework to extract the parameters b, c, and d, preliminary analysis [5,21] clearly indicates that the HTP results are much too small. The same conclusion can also be drawn at other temperatures.

Similar statements can be made for the parameter d which differs even more dramatically in two theories.

TABLE VIII. Semiclassical results for the interference parameters c, b, and d of HD perturbed by He.

Transition	c (amagat^{-1})	b (amagat^{-2})	d (amagat^2)
	$T=77$ K		
$R(0)$	-1.2×10^{-3}	2.3×10^{-6}	-2.0×10^{-6}
$R(1)$	5.4×10^{-5}	4.5×10^{-6}	1.2×10^{-7}
$R(2)$	2.6×10^{-3}	9.2×10^{-6}	5.5×10^{-6}
	$T=195$ K		
$R(0)$	-1.5×10^{-3}	2.3×10^{-6}	-3.3×10^{-6}
$R(1)$	-1.3×10^{-3}	6.0×10^{-6}	-3.3×10^{-6}
$R(2)$	-3.1×10^{-4}	1.0×10^{-5}	-8.2×10^{-7}
	$T=295$ K		
$R(0)$	-1.5×10^{-3}	1.8×10^{-6}	-3.8×10^{-6}
$R(1)$	-1.9×10^{-3}	6.3×10^{-6}	-5.1×10^{-6}
$R(2)$	-1.1×10^{-3}	1.2×10^{-5}	-3.5×10^{-6}

TABLE IX. Semiclassical results for the interference parameters c, b, and d of HD perturbed by Ar.

Transition	c (amagat^{-1})	b (amagat^{-2})	d (amagat^{-2})
	$T=77$ K		
$R(0)$	-3.3×10^{-4}	2.9×10^{-6}	-1.5×10^{-6}
$R(1)$	1.5×10^{-3}	7.0×10^{-6}	3.8×10^{-6}
$R(2)$	1.3×10^{-2}	3.8×10^{-5}	4.2×10^{-5}
	$T=195$ K		
$R(0)$	1.1×10^{-3}	2.0×10^{-6}	-8.4×10^{-7}
$R(1)$	-2.1×10^{-4}	4.5×10^{-6}	-8.6×10^{-7}
$R(2)$	1.3×10^{-3}	1.7×10^{-5}	5.1×10^{-6}
	$T=295$ K		
$R(0)$	1.9×10^{-3}	1.1×10^{-6}	-2.8×10^{-7}
$R(1)$	-8.9×10^{-5}	3.4×10^{-6}	-1.2×10^{-6}
$R(2)$	5.3×10^{-4}	1.5×10^{-5}	2.3×10^{-6}

However, it is easy to see from Tables VIII and IX in which we summarize our semiclassical results for parameters b, c, and d, that parameters d and b are of little importance at low density.

V. CONCLUSIONS

A general parametrization for a spectrum with interference between allowed and collisional-induced transitions is presented. Both a HTP-type (no m and J mixing) calculation and a semiclassical calculation including m- and J-mixing effects are carried out for the relevant parameters for HD-He and HD-Ar systems. Comparison of both sets of results with experimental data shows clearly the importance of m- and J-mixing effects. There remain, however, features in the experimental data that are not fully explained by the present calculation. We hope that a full quantal theory can be developed in the future that will further clarify this situation.

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