Theory of the relaxation matrix and its relation to microwave transient phenomena. II. Semiclassical calculations for systems of OCS and nonpolar collision partners*

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Cross sections corresponding to relaxation times T_1 and T_2 measured in microwave transient experiments are calculated for systems of OCS and nonpolar collision partners, employing the recently developed semiclassical theory of molecular collisions. Cases in the presence and absence of static Stark field are described. The over-all agreement with existing experimental results is encouraging. Similarities and differences between T_1/T_2 values in microwave transient experiments and in molecular beam maser experiments are discussed, together with a role of semiclassical collisional selection rules.

I. INTRODUCTION

In a previous paper[1] (which will be referred to as I), relations have been established between relaxation times T_1 and T_2 measured in low pressure microwave transient experiments, in the presence and in the absence of static fields, and various collision cross sections. In this paper the semiclassical expressions given in Sec. VI of Part I are applied to study the collision dynamics of the systems of OCS and various collision partners and the results are compared with the available experimental data. In the analysis, comparison is also made between the results of microwave transient and molecular beam maser experiments, and a role of collisional selection rules, which occur semiclassically but not classically, is described.

II. THE INTERMOLECULAR POTENTIAL

The intermolecular potential between OCS and a structureless atom depends on the distance R between the centers of mass of the atom and OCS, and on the angle χ between R and the molecular axis of OCS (Fig. 1).

Let $\mathbf{j}$ be the classical rotational angular momentum of OCS, $\mathbf{l}$ the orbital angular momentum for the relative motion, and $\mathbf{J}$ the total angular momentum defined by the vector equation $\mathbf{J}=\mathbf{l}+\mathbf{j}$. Let the magnitudes of these angular momenta be $\hat{l}$, $\hat{j}$, and $\hat{J}$. The calculation of classical trajectories is to be specified by these quantities $\hat{l}$, $\hat{j}$ and $\hat{J}$, and their conjugate angle variables q_l, q_j and q_J (Fig. 2 of I). χ is related to these action-angle variables by[2]

$$\cos\chi=\cos q_l\cos q_j+[(\hat{J}^2-\hat{l}^2-\hat{j}^2)/2\hat{l}\hat{j}]\sin q_l\sin q_j\,. \quad (2.1)$$

When London dispersion forces are mainly responsible for the anisotropic intermolecular interaction,[3] the potential is estimated to be[4,5]

$$V(R,\chi)=4\epsilon\{(\sigma/R)^{12}-(\sigma/R)^6[1+a_p P_2(\cos\chi)]\}\,. \quad (2.2)$$

In this equation, a_p is calculated from the formula[6]

$$a_p=(\alpha'-\alpha'')/(\alpha'+2\alpha'')\,, \quad (2.3)$$

where α' and α'' are the longitudinal and transverse polarizabilities of the linear molecule. From the values given in Ref. 7, a_p is found to be 0.28 for OCS. The quantities σ and ϵ in Eq. (2.2) are estimated from the usual combination rules for the Lennard-Jones parameters[6b]:

$$\sigma=\tfrac{1}{2}(\sigma_{OCS}+\sigma_X) \quad (2.4)$$

$$\epsilon=(\epsilon_{OCS}\epsilon_X)^{1/2}\,, \quad (2.5)$$

where X refers to the perturbing atom. From Ref. 6(b), it is found that $\epsilon=58.5$ °K, $\sigma=3.35$ Å for OCS–He and $\epsilon=204$ °K, $\sigma=3.87$ Å for OCS–Ar.

III. CALCULATION OF CROSS SECTIONS

The cross sections $\sigma^K_{f'i',fi}$ to be calculated are related to the corresponding relaxation matrix elements by Eq. (6.1) of I:

$$\Lambda^K_{f'i',fi}=N\langle v\sigma^K_{f'i',fi}\rangle\,, \quad (3.1)$$

where i and f denote the angular momentum quantum numbers j_i and j_f of the absorber before and after light absorption and before a collision, while i' and f' denote their values after a collision. N is the number density of the perturbing gas, and $\langle\cdots\rangle$ denotes a thermal average:

$$\langle v\sigma^K_{f'i',fi}\rangle=\int_0^\infty 4\pi v^2 dv\,\rho_v(v\sigma^K_{f'i',fi})\,. \quad (3.2)$$

Here, v is the relative velocity for the absorber–perturber pair and

$$\rho_v=(\mu/2\pi k_B T)^{3/2}\exp(-\mu v^2/2k_B T)\,. \quad (3.3)$$

The relevant formulas for computing $\sigma^K_{f'i',fi}$ in the general case are discussed in Sec. VI of I.

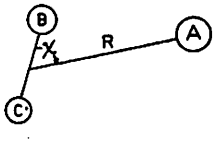

FIG. 1. Relative coordinates for describing atom–rotor collision.

From Eq. (2.2), it is observed that the potential is invariant under one or both of the following transformations:

$$q_i \to q_i + \pi\,, \qquad q_j \to q_j + \pi\,. \tag{3.4}$$

Hence, one only has to consider q_i and q_j in the interval from 0 to π and symmetry considerations[8,9] reduce the cross section given by Eq. (6.8) of I to

$$\sigma^K_{j'_i,j_i} = \int_0^\infty 2\pi b\, db\, S(b) \tag{3.5}$$

$$S(b) = \int_0^\pi \frac{d\bar{q}_1}{\pi} \int_{|J-l|}^{\hat{J}+\hat{l}} d\hat{J}\, \frac{\hat{J}}{2\hat{l}\hat{j}} (\delta_{j'_f j_f}\delta_{j'_i j_i} - P_{\hat{j}',\hat{j}})\,. \tag{3.6}$$

Throughout this paper, $\hbar$ is set equal to unity. $\hat{J}$, $\hat{l}$, and $\hat{j}$ in (3.6) denote the initial values of these variables before a collision; the final values are denoted by primes; b is the impact parameter defined by

$$b = \hat{l}/p_R\,, \tag{3.7}$$

where p_R is the magnitude of the radial component of the relative translational momentum. For the usual semiclassical reason,[10,11] $\hat{j}$, $\hat{l}$, and $\hat{J}$ equal $j+\frac{1}{2}$, $l+\frac{1}{2}$, and $J+\frac{1}{2}$; j and J denote the means $\frac{1}{2}(j_i+j_f)$ and $\frac{1}{2}(J_i+J_f)$, respectively; $P_{\hat{j}',\hat{j}}$ is a transition probabilitylike complex-valued term whose primitive semiclassical value is[12]

$$P_{\hat{j}',\hat{j}}(\bar{q}_1,\hat{J},b,v) = 4\sum_{\alpha,\gamma} \left|\partial\hat{j}'/\partial(\bar{q}_1/2\pi)\right|^{-1} D^{K*}_{\delta'\delta}(\alpha\beta\gamma)\,, \tag{3.8}$$

where the sum is over stationary phase points in a π interval in $\bar{q}_j$ space, and where the quantities on the RHS are evaluated along trajectories with initial angular momentum $\hat{j}$ equal to $\frac{1}{2}(\hat{j}_i+\hat{j}_f)$ and final angular momentum $\hat{j}'$ equal to $\frac{1}{2}(\hat{j}'_i+\hat{j}'_f)$. $D^{K*}_{\delta'\delta}(\alpha\beta\gamma)$ is the complex conjugate of the rotation matrix $D^K_{\delta'\delta}(\alpha\beta\gamma)$,[13] and δ', δ are equal to $j'_f-j'_i$ and j_f-j_i, respectively. β is the reorientation angle of the vector j (whose magnitude is $\hat{j}$) due to collision, and α and γ describe the collision phase shift. These angles are given in Eq. (6.11) of I in terms of the properties of the trajectory. (They are also given in Figs. 2 and 3 of I.)

A. Application to T_2

For the spectral transition $i \to f$, T_2 for absorption in the absence of static fields is given by Eq. (4.32) of I, which yields

$$1/T_2 = \mathrm{Re}\ \Lambda^1_{j_i,j_i}\,, \tag{3.9}$$

and for the case of linear molecules it involves the cross section $\sigma^K_{j_i,j_i}$ with $K=1$. From the spectroscopic selection rule $j_f-j_i=1$, $j'_f-j'_i=1$, one sets $\delta=\delta'=1$ in Eq. (3.8). For absorption or emission experiments performed in the presence of a static field, Eqs. (4.37) and (4.42) of I indicate that a linear combination of cross sections of various K's is required. In particular, for the $(j_i,m_i)=(1,\pm1)\to(j_f,m_f)=(2,\pm1)$ transition, Eqs. (4.37) and (4.42) of I give

$$1/T_2 = \mathrm{Re}\left(\tfrac{3}{5}\Lambda^1_{j_i,j_i} + \tfrac{2}{5}\Lambda^3_{j_i,j_i}\right), \tag{3.10}$$

while T_2 of the $(j_i,m_i)=(1,0)\to(j_f,m_f)=(2,0)$ transition is given by Eq. (4.8) of I:

$$1/T_2 = \mathrm{Re}\left(\tfrac{2}{5}\Lambda^1_{j_i,j_i} + \tfrac{3}{5}\Lambda^3_{j_i,j_i}\right). \tag{3.11}$$

Hence, the $K=1$ and $K=3$ cross sections are required for these transitions.

B. Application to T_1

1. General

Here, the cross sections corresponding to T_1 are considered. From (3.37) of I, for the $i\to f$ transition,

$$1/T_1 = \tfrac{1}{2}(\Lambda_{ii,ii} - \Lambda_{ff,ii} + \Lambda_{ff,ff} - \Lambda_{ii,ff})\,. \tag{3.12}$$

According to Eq. (2.2) of I, $\Lambda_{ff,ii}$ and $\Lambda_{ii,ff}$ are proportional to the S-matrix elements S_{fi} and S_{if}. However, symmetry considerations[8,9] on the particular form of the intermolecular potential (2.2) impose the collisional selection rule $\Delta j = 0, 2, 4, \ldots$. Since j_f-j_i equals unity for dipole radiation, S_{fi} vanishes. Thus, $\Lambda_{ff,ii}$, and similarly $\Lambda_{ii,ff}$ equal zero for any system whose intermolecular potential is invariant under one or both transformations of (3.4), i.e., has the property that $V(R,\chi) = V(R,\pi-\chi)$. For such systems, therefore,

$$1/T_1 = \tfrac{1}{2}(\Lambda_{ii,ii} + \Lambda_{ff,ff})\,. \tag{3.13}$$

For the Λ's in Eq. (3.13), δ and δ' in Eq. (3.8) are both zero (they involve $j_i-j_i=0$, etc). Since $D^K_{00}(\alpha\beta\gamma)$ equals the reduced rotation matrix $d^K_{00}(\beta)$, the cross sections contributing to Eq. (3.13) are not affected by the rotational phase shifts α and γ.

2. Absorption experiments in the absence of static fields

For these experiments described in Sec. V.A of I, Footnotes 35 and 36 of I show that to a good approximation, only the $K=0$ cross section is needed for T_1 except for the $j=0\to1$ transition. For the $j=0\to1$ transition, the expression for T_1 given in Footnote 35 of Part I is

$$1/T_1 = \tfrac{1}{2}[\langle\langle 00,00|\Lambda|00,00\rangle\rangle + \langle\langle 10,10|\Lambda|10,10\rangle\rangle] = \tfrac{1}{2}[\Lambda^0_{00,00} + \tfrac{1}{3}\Lambda^0_{11,11} + \tfrac{2}{3}\Lambda^2_{11,11}]\,, \tag{3.14}$$

where the collisional selection rule discussed above and Eq. (4.8) of I have been used.

3. Pulse experiments

For pulse experiments discussed in Sec. V.C of I, T_1 is given by Eq. (5.3) of I for $m=0$ and by Eq. (4.43) of I for $m\neq0$. For the $j=0\to1$ case where the $(j,m)=(0,0)\to(1,0)$ transition is excited by the first π-pulse, T_1 is again given by (3.14) above, and both the transient absorption experiment and the pulse method give the same T_1. For the $j=1\to2$ case, if the $(j,m)=(1,0)\to(2,0)$ transition is pumped by the π-pulse, T_1 is given by (5.3) of I:

$$1/T_1 = \tfrac{1}{2}[(\tfrac{1}{3}\Lambda^0_{11,11} + \tfrac{2}{3}\Lambda^2_{11,11}) + (\tfrac{1}{5}\Lambda^0_{22,22} + \tfrac{2}{7}\Lambda^2_{22,22} + \tfrac{18}{35}\Lambda^4_{22,22})]\,, \tag{3.15}$$

while if the $(j,m)=(1,\pm1)\to(2,\pm1)$ transition is pumped by the π-pulse, T_1 is given by Eq. (4.43) of I:

$$1/T_1 = \tfrac{1}{2}[(\tfrac{3}{5}\Lambda^0_{11,11} + \tfrac{1}{5}\Lambda^2_{11,11}) + (\tfrac{2}{5}\Lambda^0_{22,22} + \tfrac{1}{7}\Lambda^2_{22,22} + \tfrac{18}{35}\Lambda^4_{22,22})] . \quad (3.16)$$

In Eqs. (3.15) and (3.16), the collisional selection rule discussed above has been used.

When the K-dependence of the Λ's in (3.14)–(3.16) is small, we have $1/T_1 \cong \frac{1}{2}(\Lambda^0_{00,00} + \Lambda^0_{11,11})$ for (3.14) and $1/T_1 \cong \frac{1}{2}(\Lambda^0_{11,11} + \Lambda^0_{22,22})$ for (3.15) and (3.16).

4. Semiclassical expressions

The required cross section can be written explicitly from Eqs. (3.5), (3.6), and (3.8) as

$$\sigma^K_{ii,ii} = \pi \int_0^\infty 2bdb \int_0^\pi \frac{d\bar{q}_1}{\pi} \int_{|\hat{j}-\hat{i}|}^{\hat{j}+\hat{i}} d\hat{J}(\hat{J}/2\hat{i}\hat{j})(1 - P_{\hat{j},\hat{j}}) , \quad (3.17)$$

where now the primitive semiclassical value for $P_{\hat{j},\hat{j}}$ is

$$P_{\hat{j},\hat{j}}(\bar{q}_1, \hat{J}, b, v) = 4 \sum_{\delta,\delta'} |\partial \hat{j}'/\partial \bar{q}_j|^{-1} d^K_{00}(\beta) . \quad (3.18)$$

Here $\hat{j} = \hat{j}_i$ and the substition $\delta = \delta' = 0$ has been made. When $K = 0$, $d^0_{00}(\alpha\beta\gamma) = 1$ and neither reorientation nor rotational phase shift enters into the cross section.

In Eqs. (3.8) and (3.18), it is assumed that real stationary phase points exist. For cases where no real stationary phase points exist but where the final rotational angular momentum does come close to the stationary phase value, the factor

$$\sum_{\delta,\delta'} |\partial \hat{j}'/\partial \bar{q}_j|^{-1}$$

in the above expressions is replaced by the uniform approximation value

$$2\pi |\partial \hat{j}'/\partial \bar{q}_j|^{-1} \rho^{1/2} \mathrm{Ai}^2(\rho) ,$$

as discussed at the end of Sec. VI of I.

There are situations, however, when the primitive semiclassical transition probability defined by Eq. (3.8) is greater than 1, which is physically unrealistic. For such cases, a uniform approximation might be invoked, as has been done in some other rotational energy transfer problems studied in this laboratory.[12] However, for present purposes, a simpler procedure suffices, namely to replace Eq. (3.8) in those cases by

$$P_{\hat{j}',\hat{j}} = \sum_{\delta,\delta'} |\partial \hat{j}'/\partial \bar{q}_j|^{-1} D^{K*}_{\delta'\delta}(\alpha\beta\gamma) \Big/ \sum_{\delta,\delta'} |\partial \hat{j}'/\partial \bar{q}_j|^{-1} . \quad (3.19)$$

Finally, it is convenient to define an effective cross section by

$$\bar{\sigma}^K_{j_i' j_f, j_i j_f} = \langle v \sigma^K_{j_i' j_f, j_i j_f} \rangle / \langle v \rangle , \quad (3.20)$$

where $\langle v \rangle = (8k_B T/\pi\mu)^{1/2}$ is the average thermal velocity.

IV. RESULTS

To obtain the cross sections, the classical equations of motion were integrated numerically, using the potential given by Eq. (2.2). Integration was performed in Cartesian coordinates rather than in action angle coordinates, because of the low j values considered here. (At low j's, j can become small at some points along the trajectory and the angle variables would then become ill-defined.)

A. Cross section for T_2 processes

Effective cross sections defined by Eq. (3.20) were calculated by a Monte Carlo procedure summarized in the Appendix. It is convenient to define a cross section $\sigma(T_2)$ for T_2 by

$$1/T_2 = N \langle v \rangle \sigma(T_2) . \quad (4.1)$$

First, the case of absorption with no static field present was treated. Comparing (4.1) with Eqs. (3.1), (3.9), and (3.20), one finds

$$\sigma(T_2) = \mathrm{Re}\ \bar{\sigma}^1_{j_i, j_f} , \quad (4.2)$$

where Re indicates that the real part is taken. Thus, only the cross section with $K = 1$ is needed. The results of the OCS–Ar and OCS–He systems for both the $j = 0 \rightarrow 1$ and $1 \rightarrow 2$ transitions are given in Table I, together with experimental results from linewidth measurements.

To investigate the dependence of the collisional process on impact parameter, a velocity-averaged partial cross section is defined:

$$\bar{S}(b) = \mathrm{Re} \langle v S(b) \rangle / \langle v \rangle , \quad (4.3)$$

where $\langle \cdots \rangle$ denotes an average over the Maxwell–Boltzmann distribution of relative velocity [cf. Eqs. (3.2) and (3.3)] and $S(b)$ is defined by Eq. (3.6). $\bar{S}(b)$ was evaluated at various impact parameters for both the OCS–Ar and OCS–He systems for the $j = 1 \rightarrow 2$ transition and the results are plotted in Fig. 2.

Calculations of $\sigma(T_2)$ using (4.2) for the OCS–H_2, OCS–CO_2, and OCS–N_2 systems have also been performed for the case that the perturbers are treated as structureless. The potential of Eq. (2.2) was then used with the parameters in it estimated the same way as for OCS–Ar and OCS–He using the combination rules (2.4) and (2.5). The values of ϵ and σ for use in Eq. (2.2) were $\epsilon = 111$ °K and $\sigma = 3.55$ Å for the OCS–H_2 system, 252 °K and 4.31 Å for the OCS–CO_2 system, and 126 °K and 3.99 Å for the OCS–N_2 system. The results are summarized in Table I, together with experimental measurements[3,14–16] from linewidths.

TABLE I. Cross sections for T_2 processes at $T \approx 300$ °K.

System	Spectral transition $j_i \rightarrow j_f$	$\sigma(T_2)$ (measured) (Å^2)	$\sigma(T_2)$ (calculated) (Å^2)
OCS–CO_2	$0 \rightarrow 1$	200[a]	195 ± 16
OCS–N_2	$0 \rightarrow 1$	149[a]	124 ± 9
OCS–Ar	$0 \rightarrow 1$	...	143 ± 11
OCS–Ar	$1 \rightarrow 2$	125,[b] 91 ± 4[c]	146 ± 12
OCS–H_2	$0 \rightarrow 1$	66[a]	44 ± 5
OCS–He	$0 \rightarrow 1$	49.2 ± 1.2[d]	33 ± 3
OCS–He	$1 \rightarrow 2$	30,[e] 46.8 ± 1.4[f]	29 ± 3

[a]Reference 16.
[b]References 4 and 15.
[c]Reference 3(b).
[d]Reference 20(a).
[e]References 4 and 14.
[f]Reference 20(b).

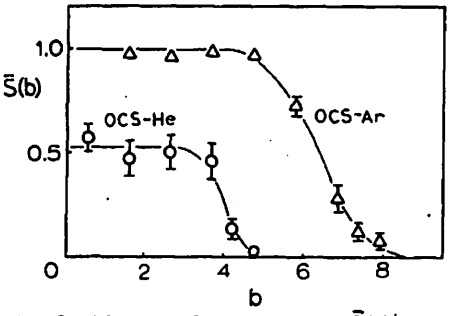

FIG. 2. The partial cross section $\bar{S}(b)$ versus impact parameter b (in Å).

Next, the case of absorption or emission in the presence of a static Stark field is considered. From Eq. (3.10), the cross section for the $(j_i, m_i) = (1, \pm 1) \rightarrow (j_f, m_f) = (2, \pm 1)$ transition is given by

$$\sigma(T_2) = \mathrm{Re}(\tfrac{3}{5}\bar{\sigma}^1_{fi,fi} + \tfrac{2}{5}\bar{\sigma}^3_{fi,fi}) , \quad (4.4a)$$

while that for the $(j_i, m_i) = (1, 0) \rightarrow (j_f, m_f) = (2, 0)$ transition is given by

$$\sigma(T_2) = \mathrm{Re}(\tfrac{2}{5}\bar{\sigma}^1_{fi,fi} + \tfrac{3}{5}\bar{\sigma}^3_{fi,fi}) . \quad (4.4b)$$

Both $\bar{\sigma}^1_{fi,fi}$ and $\bar{\sigma}^3_{fi,fi}$ were calculated for both OCS–Ar and OCS–He systems and the results are listed in Table II.

B. Cross sections for T_1 processes

A cross section $\sigma(T_1)$ for T_1 can be defined by

$$1/T_1 = N\langle v\rangle \sigma(T_1) . \quad (4.5)$$

Then, from Eqs. (3.1), (3.13), and (3.20), one has, for the $i \rightarrow f$ spectral transition for a transient absorption experiment performed in the absence of a static field,

$$\sigma(T_1) = \tfrac{1}{2}(\bar{\sigma}^0_{ii,ii} + \bar{\sigma}^0_{ff,ff}) , \quad i,f \neq 0, 1 . \quad (4.6)$$

For the $j = 0 \rightarrow 1$ transition, (3.14) gives

$$\sigma(T_1) = \tfrac{1}{2}(\bar{\sigma}^0_{00,00} + \tfrac{1}{3}\bar{\sigma}^0_{11,11} + \tfrac{2}{3}\bar{\sigma}^2_{11,11}) . \quad (4.7)$$

For T_1 measured by the pulse technique when the $(j, m) = (1, 0) \rightarrow (2, 0)$ transition is excited by the π-pulse, (3.15) gives

$$\sigma(T_1) = \tfrac{1}{2}[(\tfrac{1}{5}\bar{\sigma}^0_{11,11} + \tfrac{2}{5}\bar{\sigma}^2_{11,11}) + (\tfrac{1}{5}\bar{\sigma}^0_{22,22} + \tfrac{2}{7}\bar{\sigma}^2_{22,22} + \tfrac{18}{35}\bar{\sigma}^4_{22,22})] . \quad (4.8)$$

When the $(j, m) = (1, \pm 1) \rightarrow (2, \pm 1)$ transition is pumped by the π-pulse, (3.16) gives

$$\sigma(T_1) = \tfrac{1}{2}[(\tfrac{2}{5}\bar{\sigma}^0_{11,11} + \tfrac{1}{3}\bar{\sigma}^2_{11,11}) + (\tfrac{2}{5}\bar{\sigma}^0_{22,22} + \tfrac{1}{7}\bar{\sigma}^2_{22,22} + \tfrac{18}{35}\bar{\sigma}^4_{22,22})] . \quad (4.9)$$

TABLE II. Calculated cross sections (in Å^2) for T_2 for different m-transitions. $T = 300$ °K.

System	$\mathrm{Re}(\bar{\sigma}^1_{if,if})$	$\mathrm{Re}(\bar{\sigma}^3_{if,if})$	$\sigma(T_2)$ for $(j,m) = (1,\pm 1) \rightarrow (2,\pm 1)$ transition	$\sigma(T_2)$ for $(j,m) = (1,0) \rightarrow (2,0)$ transition
OCS–Ar	146 ± 12	162 ± 14	152	156
OCS–He	29 ± 3	38 ± 4	33	34

TABLE III. Calculated cross sections $\bar{\sigma}^K_{ii,ii}$ (in Å^2) used to calculate T_1. $T = 300$ °K.

System	$\bar{\sigma}^0_{00,00}$	$\bar{\sigma}^0_{11,11}$	$\bar{\sigma}^2_{11,11}$	$\bar{\sigma}^0_{22,22}$	$\bar{\sigma}^2_{22,22}$	$\bar{\sigma}^4_{22,22}$
OCS–Ar	146 ± 13	135 ± 11	149 ± 13	125 ± 11	137 ± 11	144 ± 12
OCS–He	35 ± 4	26 ± 3	43 ± 4	29 ± 3	38 ± 4	44 ± 4

Effective cross sections $\bar{\sigma}^K_{ii,ii}$, defined in Eq. (3.17) for $j_i = 0$, 1, and 2 of both OCS–He and OCS–Ar systems, were calculated and are summarized in Table III. Using Eqs. (4.6)–(4.9), $\sigma(T_1)$'s for the $j = 0 \rightarrow 1$ and $j = 1 \rightarrow 2$ spectral transitions for various experiments were evaluated, and are summarized in Table IV together with the values of $\sigma(T_2)$ corresponding to the same spectral transitions.

V. DISCUSSION

Considering the approximate nature of the treatment for the nonpolar molecules (H_2, CO_2, N_2) in Table I, the agreement between experimental and calculated values of T_2 is surprisingly good for systems with the larger cross sections. It was noted in Part I that the expression for $1/T_2$ in terms of relaxation matrix elements is also equal to that for the linewidth measured in line broadening experiments under nonsaturation conditions. Such equivalence has been demonstrated experimentally for the OCS self-broadening experiments for the $j = 1 \rightarrow 2$ transition.[17,18] That some of the calculated values in Table I are below the experimental results, particularly at low cross sections, is perhaps an indication that additional reinforcing anisotropic interaction terms are present, in addition to the one in the potential (2.2).

The T_2's for transitions listed in Table II for each system studied under a static Stark field are about equal. One can see from Eqs. (3.10) and (3.11) that it is unlikely that any m-dependence would be observed: $\Lambda^1_{21,21}$ and $\Lambda^3_{21,21}$ are not very different in value for the cases treated, and the weight factors in Eqs. (3.10) and (3.11)

TABLE IV. Comparison of calculated cross sections for T_1 and T_2. $T = 300$ °K.

System	Spectral transition	$\sigma(T_1)$ (Å^2)	$\sigma(T_2)$ (Å^2)
A. When the m-levels are degenerate:			
OCS–Ar	$j = 0 \leftrightarrow 1$	145[a]	143[b]
OCS–Ar	$j = 1 \leftrightarrow 2$	130[c]	146[b]
OCS–He	$j = 0 \leftrightarrow 1$	36[a]	33[b]
OCS–He	$j = 1 \leftrightarrow 2$	28[c]	29[b]
B. When the m-degeneracy is lifted by a Stark field:			
OCS–Ar	$(j,m) = (1,0) \leftrightarrow (2,0)$	141[d]	156[e]
OCS–Ar	$(j,m) = (1,\pm 1) \leftrightarrow (2,\pm 1)$	138[f]	152[g]
OCS–He	$(j,m) = (1,0) \leftrightarrow (2,0)$	38[d]	34[e]
OCS–He	$(j,m) = (1,\pm 1) \leftrightarrow (2,\pm 1)$	34[f]	33[g]

[a] From Eq. (4.7).
[b] From Eq. (4.2).
[c] From Eq. (4.6).
[d] From Eq. (4.8).
[e] From Eq. (4.4b).
[f] From Eq. (4.9).
[g] From Eq. (4.4a).

tend to reduce any difference.

The physical interpretation of these weight factors, i.e., of the coefficients of $\Lambda^1_{fi,fi}$ and $\Lambda^3_{fi,fi}$ in Eqs. (3.10) and (3.11), is fairly straightforward: K (with z-component Q) is formed vectorially by [Eq. (A36) of I]

$$\mathbf{K} = \mathbf{j}_f - \mathbf{j}_i \,. \tag{5.1}$$

As discussed in Sec. IV of Part I, Q is predetermined to be zero. Now, in Eq. (3.11) the coefficients of $\Lambda^1_{fi,fi}$ and $\Lambda^3_{fi,fi}$ each equals the square of the Clebsch–Gordan coefficient $\langle j_f, m_f; j_i, m_i | K, Q \rangle$, i.e., of $\langle 2,0;1,0|1,0\rangle$ and $\langle 2,0;1,0|3,0\rangle$, respectively, and is the probability of finding $K=1$ and $K=3$, respectively, when both $\mathbf{j}_i$ and $\mathbf{j}_f$ have z-component equal to zero. In Eq. (3.10), the coefficient of $\Lambda^1_{fi,fi}$ ($\Lambda^3_{fi,fi}$) equals the sum of the square of the Clebsch–Gordan coefficients $\langle 2,1;1,-1|1,0\rangle$ ($\langle 2,1;1,-1|3,0\rangle$) and $\langle 2,-1;1,1|1,0\rangle$ ($\langle 2,-1;1,1|3,0\rangle$) and given $Q=0$, it is the probability of finding $K=1(3)$ when $\mathbf{j}_i$, $\mathbf{j}_f$ have z-components satisfying either $m_i=1$, $m_f=-1$ or $m_i=-1$, $m_f=1$. (Even in the presence of a Stark field, the states $|j,m\rangle$ and $|j,-m\rangle$ are degenerate, and one has equal *a priori* probabilities of finding $m_i=-1$, $m_f=1$ and $m_i=1$, $m_f=-1$.)

One assumption made in phenomenologically treating the data in terms of only two relaxation times T_1 and T_2 was seen in Part I to be that the collision dynamics of the i and f states are fairly similar. The reasonableness of this approximation is apparent from the absence of any major dependence of the calculated cross sections in Tables I and III on j_i (cf. also the data in Ref. 19) when j_i is varied by one unit.

As in the case of T_2, no major m-dependence of T_1 was found in the calculations (Table IV). The reasons are similar to those for the absence of m-dependence of T_2. Furthermore, while the values of T_1 and T_2 for the $1 \rightarrow 2$ transition observed in the absence of static fields are similar to those observed in the presence of a Stark field for OCS–Ar, this is only approximately true for OCS–He (Table IV). Except for the $0 \rightarrow 1$ transition, which is a true 2-level system, comparisons of Eq. (3.15) or (3.16) with Eq. (4.32) of I and of Eq. (3.10) or (3.11) with (3.9) show that unless the K-dependence of the relaxation matrix is small (which is the case for OCS–Ar), T_1 and T_2 measured in transient absorption experiments in the absence of static field would differ from those measured in transient emission or pulse method in the presence of a Stark field.

We turn next to the relation between T_1 and T_2. It has been observed experimentally that the values of T_1 and T_2 for the OCS–He system are about the same.[20] Results of the present calculations given in Table IV agree with this observation. This result that $T_1 \approx T_2$ is also expected directly from a comparison of the expressions for T_2 and T_1: Specifically, we first note that T_1 is given by (3.12) and T_2 by (3.10), with Λ being given originally in terms of the S-matrix elements by Eq. (2.2) of I:

$$\Lambda_{f'i',fi} = (N/2\pi) \sum_a \int dE_a \rho_a (\delta_{ff'}\delta_{ii'} - \sum_{a'} S_{fa',fa} S^*_{ia',ia}) \,, \tag{5.2}$$

where a and a' denote the states of the perturber (and include those of the relative motion). From these equations we see that

$$\frac{1}{T_1} = (N/2\pi) \sum_a \int dE_a \rho_a \Big[1 - \frac{1}{2} \sum_{a'} (|S_{ia',ia}|^2 + |S_{fa',fa}|^2 - |S_{fa',ia}|^2 - |S_{ia',fa}|^2)\Big] \tag{5.3}$$

$$\frac{1}{T_2} = (N/2\pi) \sum_a \int dE_a \rho_a \Big[1 - \frac{1}{2} \sum_{a'} (S_{fa',fa} S^*_{ia',ia} + S^*_{fa',fa} S_{ia',ia})\Big] . \tag{5.4}$$

Apart from usually relatively minor reorientation and phase shift effects, these weighted averages of $S_{fa',fa} \times S^*_{ia',ia}$ and $S^*_{fa',fa} S_{ia',ia}$ are each approximately equal to that of $|S_{ia',ia}|^2$ (and $|S_{fa',fa}|^2$), when the collision dynamics of the i and f states are approximately similar. Equation (5.4) then becomes

$$\frac{1}{T_2} \cong \frac{N}{2\pi} \sum_a \int dE_a \rho_a [1 - |S_{ii}(a)|^2] \,, \tag{5.5}$$

where $|S_{ii}(a)|^2$ denotes $\sum_{a'} |S_{ia',ia}|^2$. For this case of similar collision dynamics of the i and f states, the first and second weighted averages of the S-matrix elements in (5.3) are approximately equal, as are those of the third and fourth. Thus,

$$\frac{1}{T_1} \cong \frac{N}{2\pi} \sum_a \int dE_a \rho_a [1 - |S_{ii}(a)|^2 + |S_{fi}(a)|^2] \,, \tag{5.6}$$

where $|S_{fi}(a)|^2$ denotes $\sum_{a'} |S_{fa',ia}|^2$. Using unitarity of the S-matrix the bracketted terms in (5.5) and (5.6) are found to equal $\sum_{k \neq i} |S_{ki}(a)|^2$ and $(\sum_{k \neq i} |S_{ki}(a)|^2 + |S_{fi}(a)|^2)$, respectively. Thus, the physical difference between T_1 and T_2 is evident from (5.5) and (5.6): All collisions which are inelastic with respect to the absorber's internal state contribute to T_2, whereas the inelastic collisions which contribute to $|S_{fi}(a)|^2$, i.e., which doubly contribute to reducing the difference in populations of the i and f states to its equilibrium value are doubly effective in contributing to T_1. (The other collisions are only "singly" effective.) We shall denote the weighted averages of $|S_{ii}(a)|^2$ and $|S_{fi}(a)|^2$ present in (5.5) and (5.6) by $\langle |S_{ii}(a)|^2 \rangle_{av}$ and $\langle |S_{fi}(a)|^2 \rangle_{av}$, respectively.

Thus, one sees from (5.5) and (5.6) that, according as the term $\langle |S_{fi}(a)|^2 \rangle_{av}$ is relatively small or relatively large, T_1 will be approximately equal to or appreciably smaller than T_2, respectively. In the present case, it vanished by virtue of the selection rule $\Delta j = 0, \pm 2, \pm 4, \ldots$, which in turn arose from the $P_2(\cos\chi)$ potential in (2.2). (These collisional selection rules arise from quantum mechanical interferences. The first semiclassical description was given in Ref. 8. They occur semiclassically but not classically.) If instead, a $P_1(\cos\chi)$ term were the dominant anisotropic one in the potential, the collisional selection rule would be $\Delta j = 0, \pm 1, \pm 3, \pm 5, \ldots$ If, in this case, a collision resulted in the formation of numerous possible states, $\langle |S_{fi}(a)|^2 \rangle_{av}$ would still be small, although no longer zero. Thus, T_1 and

T_2 would still be approximately equal.

However, when a $P_1(\cos\chi)$ term dominates the anisotropy and when at the same time essentially only $\Delta j \cong 0, \pm 1$ prevails in collisions, $\langle |S_{fi}(a)|^2 \rangle_{av}$ can become relatively large, and then T_1 would differ considerably from T_2. Other things being equal, small excitations ($\Delta j \cong 0, \pm 1$) will tend to be the more likely the larger the value of $\omega_{rot}\tau_{coll}$, where ω_{rot} is the rotational frequency of the absorber and τ_{coll} is a typical duration of a collision. Since ω_{rot} increases with decreasing moment of inertia of the absorber, the ideal conditions for observing a significant difference between T_1 and T_2 are a dominant $P_1(\cos\chi)$ anisotropy and a small moment of inertia of the absorber.

Experiments have been performed with OCS as absorber and CH_3F as perturber.[20] While the $P_1(\cos\chi)$ term might be a dominant one in this case, because of the large dipole moment of CH_3F, the other condition, namely that of excitation to very few states is almost certainly not fulfilled, due to the relatively large moment of inertia of OCS. (The detailed trajectory calculations used to obtain the cross sections for the systems in Table I support this view.) Experiments on systems with smaller moments of inertia would be of interest, therefore.

Both an interesting similarity and a marked difference occur between the results obtained in the microwave transient experiments[20] and those obtained in a molecular beam maser system.[21] In both cases the investigators found $T_1 \cong T_2$ for the OCS–OCS and OCS–He systems. However, while Mäder *et al.*[20] found $T_1 \cong T_2$ for OCS–CH_3F, Wang *et al.*[21] found $T_1 \cong \frac{3}{7} T_2$. It has been noted[20] that this difference in the results is not necessarily an experimental discrepancy, since the molecular beam maser experiment measures forward scattering while the other experiment measures total cross sections, and the behavior of the two could differ. We shall proceed to show, using (5.5) and (5.6), that the similarity (OCS–OCS, OCS–He) and the difference (OCS–CH_3F) in the two experimental results on T_1/T_2 are indeed in the direction expected.

First, we note that to treat the molecular beam maser experiment some changes in detail in the equations in Part I would have to be made (cf. Ref. 21), partly because of the initial rotational state selection in the beam and more importantly because one is now treating differential rather than total cross sections. Nevertheless, to make the argument we shall use (5.5) and (5.6), but summed only over the larger orbital angular momenta, namely over those corresponding semiclassically to the large impact parameters which provide the forward scattering into the detection system (cf. equation for R_{ijkl}, p. 5273 of Ref. 21). Thus, we are interested now in the average value of S-matrix elements in (5.5) and (5.6) corresponding to this range of impact parameters.

Both experiments and calculations[22,23] support the view that forward scattering involves, as expected, more elastic collisions than does that for total cross sections [cf. also the results for $\bar{S}(b)$ in Fig. 2, where $\bar{S}(b)$ is defined via (4.3), (3.5), and (3.6)]. Thus, one expects and finds[22,23] fewer final collisional states excited in the forward scattering experiment than that in the total cross section one. For example, one sees a dramatic decrease in inelastic cross sections with decreasing scattering angle in Fig. 5 of Ref. 23, the larger excitations decreasing the most. Ultimately, at sufficiently low scattering angles only one or two final postcollision states will occur. In this case, the conditions become increasingly appropriate for finding a difference between T_1 and T_2 in the molecular beam maser experiment when the OCS is perturbed by a molecule with a large dipole moment, such as CH_3F. In contrast, in the OCS–OCS and OCS–He systems, the condition that the dominant anisotropic term be a $P_1(\cos\chi)$ one is not fulfilled, judging from the equality of the T_1 and T_2 in the molecular beam experiments [and from the potential (2.2) for the OCS–He system]. In this way, the differences and the similarities of the results in the microwave transient and molecular beam maser experiments can be understood.

We turn next to the aspect of the theory of collisional line broadening regarding the behavior of the partial cross sections $\bar{S}(b)$ as a function of the impact parameter b. The results in Fig. 2 for the OCS–Ar and OCS–He systems provide information on a classification of inelastic collisions into strong or weak categories. Strong collisions are those which interrupt the radiative process completely[24,25] and so are those which change the j quantum number. Such events give zero contribution to $P_{j',j}$ in the RHS of Eq. (3.6), and contribute a value of unity to $\bar{S}(b)$. Weak collisions are those which do not affect the j quantum number but change only the reorientation and/or the phase of the rotor. They would give finite contribution to $P_{j,j}$ on the RHS of Eq. (3.6). For OCS–Ar, strong collisions dominate for impact parameters less than 5 Å, as one sees from the fact that for $b \leq 5$ Å in Fig. 2, $\bar{S}(b)$ is close to unity. For the OCS–He system, on the other hand, the results in Fig. 2 indicate that weak collisions contribute significantly even at low impact parameters. This phenomenon is not entirely unexpected, since the interaction potential for OCS–He is much weaker than that for OCS–Ar. At large impact parameters, only elastic collisions are possible, rendering the second term on the RHS of Eq. (3.6) equal to unity and thus $\bar{S}(b)$ decreases to zero at large b.

It is of interest to compare the results in Fig. 2 with an assumption commonly used in perturbative theories of line broadening.[26] In the latter case, the partial probability term [called $S_2(b)$ there] becomes unbounded when b becomes small. The general treatment then is to set $S_2(b)$ equal to unity when $b < b_0$, where b_0 is determined by the condition

$$S_2(b_0) = 1 \,. \tag{5.7}$$

One sees from Fig. 2 that such an assumption would not be unreasonable for the OCS–Ar system. It would be less accurate for the OCS–He one. The maximum in the function $2\pi b\bar{S}(b)$ is found to occur, using the results in Fig. 2, at $b \cong 5$ Å and $b \cong 3$ Å for the OCS–Ar and OCS–He systems, respectively.

Lastly, it is interesting to examine the implications of

a situation where all collisions are strong for b less than some given value, b_0, and completely ineffective for $b > b_0$; i.e., where in (5.5) and (5.6), $|S_{ii}(a)|^2$ is zero for all orbital states a corresponding to $b < b_0$, and is unity for all orbital states a corresponding $b > b_0$. Provided the collisions are sufficiently strong that $|S_{fi}(a)|^2$ is also small for $b < b_0$ (and for $b > b_0$) because of collisional excitation from state i to many possible states, one then concludes from (5.5) and (5.6) that $T_1 \cong T_2$ for this model. Several authors[17,27] have employed this strong collision assumption and hence only a single relaxation time was needed to account for saturation effects.

VI. CONCLUSIONS

The present results show that the simple potential (2.2) provides a reasonable agreement between measured and calculated cross sections for these systems of nonpolar collision partners, at least for case of the systems with the larger cross sections. The potential contains no adjustable parameters. The present calculations also indicate that any m-dependence of T_1 and T_2 would only be small (but not because of any selection rule), although calculations should be made in each case. A difference in the values of T_1 and T_2, on the other hand, would be expected when two conditions are simultaneously fulfilled: The anisotropic part of the interaction potential should have a dominant $P_1(\cos\chi)$ term, rather than mainly a P_2 term, and the moment of inertia of the absorber should be sufficiently small. In this case, a collisional selection rule of $\Delta j \cong 0, \pm 1$ would be roughly achieved, and provided $\langle |S_{fi}|^2 \rangle_{av}$ is roughly comparable with or greater than $\langle 1 - |S_{ii}|^2 \rangle_{av}$, a significant difference in T_1 and T_2 would occur. These arguments also suggest an explanation for the interesting similarity [for dominant $P_2(\cos\chi)$ systems] and the difference [for a $P_1(\cos\chi)$ system] in results of recent microwave transient and molecular beam maser experiments. In the latter, we have made use of a collisional selection rule which arises semiclassically but not classically. Finally, the concept of strong and weak collisions is discussed in the light of the results in Fig. 2.

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APPENDIX: EVALUATION OF $\langle v\sigma^K_{f'i',fi} \rangle$

Two of the integration variables, b and v in Eq. (3.17), where (3.5) and (3.6) are used for $\sigma^K_{f'i',fi}$, have an infinite domain of integration. It is desirable to transform the domain to a finite one to perform the Monte Carlo integration. A new variable x_v is introduced via

$$dx_v = -2\eta^2 v^3 \exp(-\eta v^2)\, dv\,, \tag{A1}$$

where η is $\mu/2k_BT$. Integrating (A1) and choosing $x_v = 0$ at $v = \infty$, we have as the new integration variable

$$x_v = (1 + \eta v^2)\exp(-\eta^2 v^2)\,. \tag{A2}$$

x_v goes from 1 to 0 as v goes from 0 to ∞.

It is useful to transform b to a new variable[9a]:

$$x_b = \exp(-b^2/B^2)\,, \tag{A3}$$

where B is a scaling constant. Thus,

$$dx_b = (-2b/B^2)\exp(-b^2/B^2)\, db\,, \tag{A4}$$

and x varies from 1 to 0 as b varies from 0 to ∞. The Gaussian weighting factor in (A4) resembles that in Fig. 2 and so the transformation (A3) is appropriate. Similarly, the variables x_j, related to the cosine of the angle between $\hat{l}$ and $\hat{j}$, and x_q are introduced[9a]:

$$x_j - \tfrac{1}{2} = (\hat{J}^2 - \hat{l}^2 - \hat{j}^2)/4\hat{l}\hat{j}\,, \tag{A5}$$

$$x_q = \overline{q}_i/\pi. \tag{A6}$$

Equation (3.17) for $\overline{\sigma}^K_{f'i',fi}$ becomes

$$\overline{\sigma}^K_{f'i',fi} = \int_0^1\int_0^1\int_0^1\int_0^1 (\pi B^2/x_b)[\delta_{i'i}\delta_{f'f} - P_{\hat{f}'\hat{f}}]\, dx_j dx_b dx_j dx_q. \tag{A7}$$

The integral (A7) is evaluated by averaging the integrand, denoted by f, over N points $\mathbf{x}_k$, randomly selected within a 4-dimensional unit cube where N is a large number, i.e.,

$$\overline{\sigma}^K_{f'i',fi} \simeq \frac{1}{N}\sum_{k=1}^{N} f(\mathbf{x}_k)\,. \tag{A8}$$

The error is approximately given by

$$\delta^2 = \sum_{k=1}^{N} [f(\mathbf{x}_k) - \overline{\sigma}^K_{f'i',fi}]^2/N(N-1)\,. \tag{A9}$$

In our calculation, N equals 100 and the error estimate was typically about 10%.

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