Rotational Distribution of $CO_2(00^00)$ after Collisions with Hot Atoms

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By use of the rotational distribution expression previously derived based on the collisional time correlation function formalism, the rotational distributions of CO_2 vibrational ground state (00^00) after collisions with hot H, D, or Cl atom have been constructed. Energy and rotational quantum number parameters which can characterize the rotational distributions are also calculated and compared with those deduced from the experimental distribution. The results from this work would be very useful in predicting the rotational distributions in the lower J region for which experimental data are not available due to the interference from the ambient CO_2.

Introduction

State resolved vibrational and rotational excitations resulting from the collisions between hot atoms and diatomic or triatomic molecules have been of great interest to both experimentalists and theoreticians alike.[1,2] Hydrogen or chlorine atoms with large, well-defined kinetic energy around 0.5 to 2 eV are generated by laser photolysis of small molecules such as $H_2S(D_2S)$ or Cl_2.[3] These nearly mono-energetic, translationally hot atoms are then led to collide with various target molecules, and the resulting nascent vibrationally and/or rotationally excited state populations of the scattered molecules are probed with a variety of experimental techniques. Especially interesting from a theoretical point of view are those collision systems for which product rotational state distributions are well resolved, in addition to the electronic and/or vibrational states, such as H+CO,[4,5] H(D)+CO_2,[6-16] H+NO,[17] H+H_2O,[18] and H+HF.[19]

Approximately a decade ago we derived a simple expression for the double differential cross section (with respect to scattering angles and final rotational energies) of molecules with thermal distribution of initial rotational states colliding with fast atoms.[20] This expression, based on the collisional time correlation function (CTCF) formalism,[21,22] is valid when the collision time is short compared with the periods of internal motions of target molecules. This condition is readily fulfilled when the relative translational energy is very large compared to the amount of energy transfer and the interaction potential is of repulsive type.

The formulation gave a final rotational state distribution in a simple form which can be used to parameterize the experimental results. The derived expression was applied to the experimentally measured final rotational distributions of various electronic and vibrational states, and was found to reproduce the experimental results very well. The specific collision systems analyzed theoretically by this method so far are $H^*+CO_2(00^00; J) \rightarrow H+CO_2(00^01; J')$,[20,24] $H^*+CO(v=0; J) \rightarrow H+CO(v=0, 1, 2; J')$,[20,23] $H^*+CO_2(00^00; J) \rightarrow H+CO_2(00^01, 01^11, 00^02, 10^00/02^00; J')$[24]. All molecules in these systems were in $^1\Sigma$ electronic state for which the total electronic angular momentum is zero. Rotational and/or vibrational energy transfer into CO_2 molecules have received particular interests because of its role in chemical laser and green house effect. The formulation was also extended and a slightly modified expression was obtained to include the Hund's case (a) molecules with non-zero total electronic angular momentum. This modified expression was then applied to $H^*+NO(v=0; J) \rightarrow H+NO(^2\Pi_{1/2}; v'=1; J')$ and $NO(^2\Pi_{3/2}; v'=1, 2, 3; J')$.[25]

In most cases for which vibrational and rotational excitations occur simultaneously, the final rotational state distributions were well resolved experimentally over the whole rotational quantum number (J') range, *i.e.*, from very low J' to very large J'. However, in their study of pure rotational excitation of CO_2 ground vibrational state (00^00), Hershberger *et al.* could measure the rotational state distribution after collisions with H, D or Cl only at very high J' due to the interference of the uncollided CO_2 in the sample cell.[16] To be specific, the rotational state distribution was measured only at $J' = 54, 58, 64, 66, 74,$ and 78 for $H^*(D^*)+CO_2(00^00; J) \rightarrow H(D)+CO_2(00^00; J')$ and $J' = 52, 58, 64, 66, 74, 78$ and 80 for $Cl^*+CO_2(00^00; J) \rightarrow Cl+CO_2(00^00; J')$. Furthermore, there is some theoretical controversy regarding the final rotational distribution. While Kreutz and Flynn report that the relative rotational cross-section decreases linearly from small ΔJ to large ΔJ (ΔJ being the difference between the final and the initial rotational quantum number),[26] Clare *et al.* argues that the decrease should be exponential.[27]

Therefore, it will be worthwhile to have a rotational state distribution covering the full range of the rotational quantum states from low J' to large J' and some energy parameters which can be useful in characterizing the final rotational distribution of the CO_2 (00^00) state after collisions with hot atoms. This will help guide the experimentalists in their future work. In this work we have constructed rotational distributions of CO_2 (00^00) ground vibrational state after collisions with H, D or Cl atoms by use of the CTCF based theoretical analysis and give the results below.

Theory

Since the essential features of CTCF formalism and the procedures for deriving the cross-section for scattering into a final rotational state J' are given in detail elsewhere,[20] we present here only the brief summary of the theory which is necessary to interpret the pure rotational excitation experiments.

According to the CTCF formalism,[21,22,28-32] the double differential cross section σ with respect to scattering angle Ω and the amount of energy transfer ε is given by

$$\frac{d^2\sigma}{d\varepsilon d\Omega} = \frac{d\sigma_{ev}}{d\Omega}\left(\frac{2}{\pi}\right)^{1/2}\langle(\Delta\varepsilon)^2\rangle^{-1/2}$$

$$\exp\{-(\varepsilon-\langle\varepsilon\rangle)^2/[2\langle(\Delta\varepsilon)^2\rangle]\} \qquad (1)$$

where $<\varepsilon>$ is the average energy transfer and $<(\Delta\varepsilon)^2>$ is the square of its dispersion. The averaged quantities introduced in Eq. (1) are obtained by averaging over the Fourier transform of the time correlation function.[20]

Typical collision experiments with fast atoms have been carried out using target molecules initially at thermal equilibrium. They can be analyzed for specific electronic and vibrational transitions, for which the final rotational distributions are presented as a function of the final rotational energy E_r' or quantum number J' rather than as a function of the amount of energy transfer ε in Eq. (1). Therefore, one should modify Eq. (1) to obtain an expression in terms of E_r' or J' for a cross-section which has been averaged over the initial rotational state distribution. Treating the initial rotational quantum number J as a continuous variable, one obtains

$$\frac{d^2\sigma}{dE_r'd\Omega} = \int_0^\infty \frac{d^2\sigma}{d\varepsilon d\Omega}\left(\frac{d\varepsilon}{dE_r'}\right)w_r(J)dJ \qquad (2)$$

Here unprimed and primed quantities refer to the initial and final states, respectively, and w_r refers to the distribution of initial rotational quantum state J. Since there is no electronic or vibrational transition for this case, the amount of energy transfer ε becomes

$$\varepsilon = \varepsilon_r = E_r' - E_r \qquad (3)$$

$$w_r = (2J+1)\exp[-E_r/(k_BT)] \qquad (4)$$

$$E_r = Bhc[J(J+1)] \qquad (5)$$

$$\varepsilon - \langle\varepsilon\rangle = \varepsilon_r - \langle\varepsilon_r\rangle, \quad \langle(\Delta\varepsilon)^2\rangle = \langle(\Delta\varepsilon_r)^2\rangle \qquad (6)$$

where B is the rotational constant of the molecule, h the Planck constant, and c the speed of light.

The rest of the derivation follows exactly the procedure outlined in section II. B of Reference 20. The final expression for the scattering cross-section for the final rotational state J' becomes

$$\sigma(J') = a_3(2J'+1)\exp\left(a_1 + \frac{a_2}{2} - x'\right)$$

$$\times \operatorname{erfc}[(a_1 + a_2 - x')/(\sqrt{2a_2})] \qquad (7)$$

where

$$a_1 = \langle\varepsilon_r\rangle/(k_BT) \qquad (8)$$

$$a_2 = \langle(\Delta\varepsilon_r)^2\rangle/(k_BT)^2 \qquad (9)$$

$$x' = E_r'/(k_BT) = J'(J'+1)Bhc/(k_BT) \qquad (10)$$

Therefore $\sigma(J')$ can be expressed as a function of the final rotational quantum number J' and of three parameters a_1, a_2, and a_3. The essential features of the final rotational distribution are determined solely by the parameters a_1 and a_2. The third parameter a_3 is a scaling factor which is necessary to fit the experimental distribution usually expressed in an arbitrary, relative scale.

In implementing the fitting process to the experimental data from the experimental rotational distribution, one obtains the relative population for each J' and minimizes a chi square function of the parameters $\{a_i, i = 1 \text{ to } 3\} = \boldsymbol{a}$ defined by

$$\chi^2(\boldsymbol{a}) = \sum_{J'}\left[\frac{N_{J'} - N(J';\boldsymbol{a})}{\Delta N_{J'}}\right]^2 \qquad (11)$$

where N_J' is the experimental relative population for final rotational state J', $\Delta N_J'$ is the standard deviation in the measured values of N_J', and $N(J'; \boldsymbol{a})$ is the theoretical distribution for a given set of the parameters $\mathbf{a}$. The computer program we have used requires $\Delta N_J'$'s as input together with J' and N_J'. In cases where $\Delta N_J'$ is reported only for one data point in the experiment, the same constant percentage value has been assigned to all N_J''s. One could, of course, use the same absolute $\Delta N_J'$ value for all data points. The choice, however, does not affect the final result appreciably.[24]

We have used the numerical procedure of Levenberg-Marquardt[33-35] to obtain the best fit parameters. The iterative process to obtain the best set of $\boldsymbol{a}$ values was carried out until two successive iterations gave $\chi^2(\boldsymbol{a})$'s within 10^{-3} of each other.

Results and Discussion

Hershberger *et al.* measured the rotational distribution of CO_2 in its ground vibrational state (00^00) after collisions with hot H, D or Cl atom. The initial state of CO_2 molecule

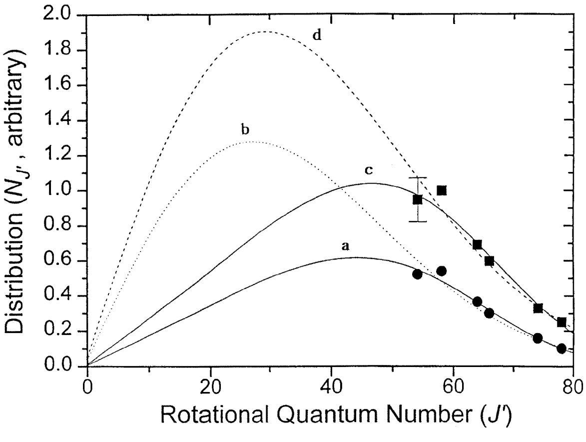

Figure 1. Rotational distribution of $CO_2(00^00)$ after collisions with hydrogen. ● H^* collision, ■ D^* collision (exp. Reference 16). Curves **a** (H^*; CTCF), **b** (H^*; Boltzmann, T=862K). **c** (D^*; CTCF), **d** (D^*; Boltzmann, T=991K).

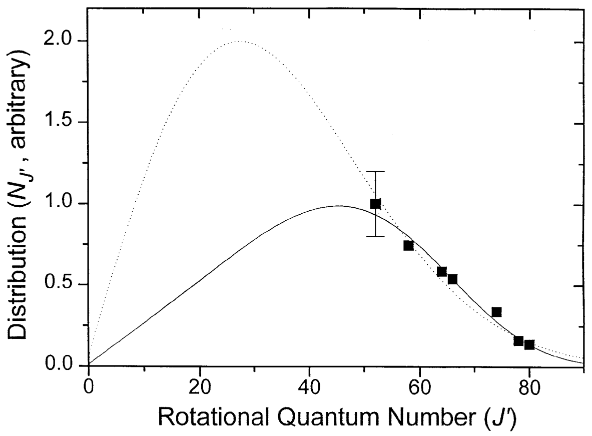

Figure 2. Rotational distribution of $CO_2(00^00)$ after collisions with chlorine. ■ (exp. Reference 16). — CTCF, ··· Boltzmann (T=876 K).

was not state-selected but at thermal equilibrium at 298K. The collision processes can be summarized as follows.

$$H^*(D^*,Cl^*) + CO_2(00^00; J) \rightarrow H(D,Cl) + CO_2(00^00; J')$$

The translational energies of the hot atoms are 2.30, 2.16 and 0.5 eV for H^*, D^* and Cl^*, respectively.

Their experimental data at high J' together with the theoretical rotational distribution curves obtained by fitting Eq. (7) to the experimental points are shown in Figures 1 and 2. For reference, best-fit Boltzmann distributions are also shown. As can be seen from the Figures, the general qualitative fit to the experimental data points is excellent in all three collision systems. The best fit parameters are $a_1 = -0.222$, $a_2 = 21.7$, $a_3 = 0.0503$ for H^* collision; $a_1 = 0.214$, $a_2 = 23.7$, $a_3 = 0.0823$ for D^* collision; $a_1 = 0.166$, $a_2 = 21.2$, $a_3 = 0.0761$ for Cl^* collision.

The best fit Boltzmann temperatures for H^*, D^* and Cl^* collisions are 862, 991 and 876K, respectively. Although the Boltzmann distributions also seem to reproduce the experimental data very well, we do not believe this to be real. Experimentally, the nascent rotational distributions of the various molecules including CO_2 after collisions with hot atoms have never shown Boltzmann type distributions;[4-19] we believe that this agreement is coincidental due to the paucity of data points, especially at lower J' states.

From their limited experimental results Hershberger *et al.*[16] could not pinpoint the exact position of the maximum rotational population of $CO_2(00^00)$ state after collision with hot atoms. All that they could say was that the distribution would peak at $J' < 58$. From the total amount of energy available for rotational excitation and based on the statistical density of states calculation, O'Neill *et al.*[7] predicted that the $CO_2(00^00)$ rotational distribution would show the maximum population at $J' = 154$ for H^* and $J' = 72$ for Cl^* collisions. The experimental results, however, clearly do not support this prediction. Our results show that J'_{max} to be 44, 46 and 46 for H^*, D^* and Cl^* collisions, respectively, and we believe that these values are much more realistic.

Table 1. Rotational state characteristics for $CO_2(00^00)$ after collisions

Hot Atom		J'_{max}	$<J'>^b$	$<E_r'>$ (in joule)	$<(\Delta E_r')^2>^{1/2}$ (in joule)
H^*	Exp.[a]	not certain		$^b\ 3.02 \times 10^{-20}$	7.19×10^{-21}
	Theory (CTCF)	44	42	$^b\ 3.03 \times 10^{-20}$	6.99×10^{-21}
				$^c\ 1.63 \times 10^{-20}$	1.16×10^{-20}
D^*	Exp.	not certain		$^b\ 3.07 \times 10^{-20}$	7.31×10^{-21}
	Theory (CTCF)	46	44	$^b\ 3.09 \times 10^{-20}$	6.97×10^{-21}
				$^c\ 1.75 \times 10^{-20}$	1.21×10^{-20}
Cl^*	Exp.	not certain		$^b\ 3.04 \times 10^{-20}$	8.71×10^{-21}
	Theory (CTCF)	46	44	$^b\ 3.05 \times 10^{-20}$	8.05×10^{-21}
				$^c\ 1.73 \times 10^{-20}$	1.25×10^{-20}

J'_{max} is the rotational quantum number at which the rotational distribution shows its maximum. $<J'>$: Average rotational quantum number, $\sum_{J'} J'N_{J'} / \sum_{J'} N_{J'}$. $<E_r'>$: Average rotational energy, $\sum_{J'} E_{J'}N_{J'} / \sum_{J'} N_{J'}$. $<(\Delta E_r'^2)>^{1/2} = (<E_r'^2> - <E_r'>^2)^{1/2}$: dispersion in rotational energy. [a]Reference 16. [b]Calculated at J''s for which experimental measurements are reported ($J' \approx$ 50-80). [c]Calculated for the full J' range (J' = 0-80).

To judge the goodness of fit quantitatively we calculated some parameters which characterize the rotational distribution such as average rotational quantum number $<J'>$, average rotational energy $<E_r'>$ and its dispersion $<(\Delta E_r')^2>^{1/2}$ and grouped them together in Table 1. J'_{max} and $<J'>$ are rounded to the nearest even number because no odd numbered rotational states are populated. For the CTCF distributions $<E_r'>$ and $<(\Delta E_r')^2>^{1/2}$ are calculated in two ways; firstly for the full J' range (J' = 0-80), and secondly for the experimental measurements range (J' = 50-80). The agreement between the experimental and theoretical results are excellent in the J' = 50-80 range. Comparison of the experimental $<E_r'>$ and $<(\Delta E_r')^2>^{1/2}$ results with the full J' range CTCF results are, of course, meaningless. The full range CTCF results are presented solely for possible future reference.

In summary, we have constructed rotational state distributions for CO_2 ground vibrational state (00^00) after collisions with hot atoms by means of CTCF based theoretical analysis. The agreement between experiment and theory is very good where the experimental results are available. We have also been able to present some parameters such as J'_{max}, $<J'>$, $<E_r'>$ and $<(\Delta E_r')^2>^{1/2}$ which can be helpful in characterizing the rotational state distributions for the whole quantum number range.

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35. Note: The subroutine MRQMIN listed in Ref. 33 should be slightly modified to prevent premature termination of the iterative process after an increase in χ^2. All one has to do is to omit the fourth from the last statement (CHISQ =OCHISQ) from the subroutine program.