A REVIEW OF VIBRATIONAL CROSS SECTIONS INVOLVING H2O, CO2, H2, CO AND He

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13. ABSTRACT Theoretical vibration cross sections calculated by Marriott using a close coupling analysis for the excitation of CO, CO_2 and H_2O in collision with CO_2, H_2O, H_2 and He are reviewed and presented in a form convenient for use in modeling the chemistry of rarefied flow environments. Although no direct cross section data is available for any of the excitation processes considered, an indirect evaluation of the theoretical values is obtained by comparison to available relaxation time measurements.

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I. Introduction

Under conditions in which the molecular velocity distribution is non-Maxwellian, the characterization of chemical processes cannot be made using rate constants but must be calculated from the fundamental inelastic cross sections. Since these non-equilibrium environments are not described by a "temperature", the excitation produced in each collision must be separated, evaluated and summed in order to evaluate the total excitation rates. In particular, for the purpose of estimating the infrared radiative emission from a collisionally excited gas when the relative collision energy is high (of the order of .25 to several eV) and the effective rotational temperature of the colliding molecules is of the order of a few hundred degrees, a cross section description is required to calculate the initial vibrational excitation. At present no experimental procedure has been publicized which will measure vibrational cross sections for neutral species of interest in the upper atmosphere polluted with rocket exhaust effluents (CO_2, H_2O, H_2, CO, O, N_2, NO, etc.). Without this experimental input, theoretical methods must be relied upon to furnish excitation cross sections for relevant vibrational modes of these atmospheric species.

Over the past 10 years, Marriott[1-8] has applied a close coupling analysis to calculate the vibration-translation (VT) cross sections for many of the internal modes of CO_2, H_2O, CO and H_2 of interest in high altitude plume studies. This report summarizes and discusses this past work and presents some new theoretical cross section data. In order to provide some experimental verification for the cross section calculations, since no direct cross section measurements are available, the cross sections have been integrated over a Boltzmann distribution of relative energies and the resulting rate coefficients compared to available rate or relaxation time measurements. This procedure is not entirely satisfactory since the current close coupling code accounts only for strong VT interactions while the thermalized energy transfer processes associated with species like H_2O and H_2 are strongly effected by vibration-rotation (VR) and, in some

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cases, vibration-vibration (VV) processes. Thus, the calculated rate coefficients are expected to be no more than a lower limit to the rate coefficients with increased agreement expected at higher temperatures where VT processes become more important due to the strong temperature dependence. This trend is found in all cases considering in this report except for the $CO_2 + H_2$ energy transfer system. For this system, it would appear that the repulsive intermolecular potential assumed in the close coupling calculation is significantly too steep. A further discussion of this case is given in the results section. The trend toward agreement between the calculated and measured rate coefficients at higher temperatures for the other transfer systems considered in this report suggests that the calculated VT cross sections are reasonably reliable for predicting the vibrational excitation of exhaust species by atmospheric constituents under conditions of high relative collision energies and low effective rotational temperatures.

In the next section, a brief account is given of the close coupling analysis and of the analysis of the theoretical cross sections in terms of rate coefficients and relaxation times. Section III presents the results of the comparison of calculated rate coefficients with available relaxation time measurements and a discussion of each energy transfer system for which calculated cross section information is available. Lastly in Section IV, a summary discussion is given of the range of reliability of the calculated cross sections based upon the calculated rate coefficients and evaluation of the approximations used in the close coupling analysis.

A complete tabulation of the excitation and de-excitation rate coefficients generated from each cross section presented in this report for the temperature range 300 to 5000 K is available directly from the author.

II. Theoretical Analysis

Since complete details of the close coupling calculation are available elsewhere[1,6], only a brief review of the method used will be given here. The excitation collision is envisioned as occurring between a structureless incident molecule and a molecule possessing internal structure characterized by its normal internal modes. The coupling between rotational and vibrational states is neglected and the scattering potential is assumed to be spherically symmetric and to be separable in terms of the vibrational and rotational coordinates, i.e. the breathing sphere model of Herzfeld, Schwartz and Slawsky[9]. For most of the cases treated in this report, the intermolecular potential is assumed to be given by the Lennard-Jones or Stockmeyer potentials[10]. The intramolecular potentials are assumed to be given by an exponentially repulsive form in which the exponential coefficient is given by the shape of the intermolecular potential at the classical turning point[9]. The vibrational wave functions are taken to be harmonic for each independent mode of vibration.

The total cross sections are obtained by summing over all significant partial waves. In general, for molecular collisions, several hundred partial waves must be taken into account. However, it has been found that the inelastic cross sections normally are slowly varying functions of the partial wave number and relatively few partial cross sections are required to permit graphical integration to be employed. The details of the close coupling equations and their method of solution are reproduced elsewhere[1].

The vibrational state designation of the polyatomic species considered in this report are given in Table I and the energies associated with the various vibrational modes are given in Table II.

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Table I.

Vibrational State Designation for Polyatomic Species

Designation	Quantum Number		
	ν_1	ν_2	ν_3
0	0	0	0
1	0	1	0
2	0	2	0
3	1	0	0
4	0	0	1

Table II.

Vibrational State Energies*

	0	1	2	3	4
CO_2	0	0.083	0.166	0.164	0.291
H_2O	0	0.198	0.395	0.441	0.465
CO	0	0.266	0.532		

*energies in eV's above the 0 state.

The direct results of these close coupling calculations produce cross sections which, for comparison with available experimental data, must be converted to Maxwellian rate coefficients. To accomplish this we note that the rate coefficients for excitation of the s to t vibrational transition is given by[11]

$$(1) \quad k_{st} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} g_t \int_0^\infty v Q_{st}(v) \exp(-mv^2/2kT) v^2 dv,$$

where m = reduced collision mass

v = relative collision speed

g_t = degeneracy of the tth state

and $Q_{st}(v)$ = cross section for the s to t process.

Detailed balancing on this process yields the relationship

$$(2) \quad k_{ts} g_t \exp(-E_t/kT) = k_{st} g_s \exp(-E_s/kT).$$

Experimentally, the relaxation time is a more frequently measured quantity. This relaxation time can be related to the excitation rate coefficient through an harmonic oscillator assumption, yielding

$$(3) \quad P\tau_{st} = \frac{RT}{k_{st}} \left[1 - \exp\left[-(E_t-E_s)/kT\right]\right]^{-1}$$

where $P\tau_{st}$ is the relaxation time in atm-sec and R is the gas constant.

In order to generate rate coefficients and relaxation times from these equations, the cross section versus energy values must be fit to an analytical function and integrated over a Boltzmann distribution of relative energies. The functional form which appears consistent with the theoretical results is

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(4) $$Q_{st}(E) = C3 * \left[\ln(E/E_T)\right]^{C2} * (E_T/E)^{C4}$$

where E = relative collision energy

E_T = threshold energy

and $Q_{st}(E)$ = cross section in cm^2.

Fitting this function to the available cross section data points has led to Table III.

For convenience in understanding the magnitude of these inelastic cross sections, the probability per collision per a given transitive $P_{st}(v)$ can be generated. This quantity is defined by

(5) $$P_{st}(v) = \frac{Q_{st}(v)}{Q_{el} + \sum_i Q_{si}(v)}$$

where Q_{el} is the elastic scattering cross section and the summation is over all available inelastic processes from the initial state s.

Application of equation (5) together with the inelastic cross section data shown in Table III and elastic scattering cross sections taken from reference 10 leads to the excitation probabilities shown in Figure 1. Note that only the probability for exciting the lowest vibrational level is shown in the Figure.

As discussed in the introduction, there are no cross section measurements with which to compare the calculated results. Therefore, the derived rate coefficients can only be compared to available experimental data. The specific reactions for which data exist are presented in the following section.

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Table III.

Coefficients to Cross Section (cm^2) vs. Energy (ev) Function

REACTION	ET (ev)	C2	C3	C4
N2 + AR Q(01)	2.89E-01	1.093E01	1.110E-23	0.0
CO + HE Q(01)	2.660E-01	3.658E00	3.263E-20	-2.147E00
CO + HE Q(02)	5.310E-01	3.659E00	8.189E-23	-4.857E00
CO + HE Q(12)	2.660E-01	3.779E00	1.299E-19	-8.742E-01
CO + H2O Q(01)	2.660E-01	1.306E01	1.449E-18	3.183E-00
CO + H2O Q(02)	5.310E-01	1.175E01	2.189E-20	1.764E-00
CO + H2O Q(12)	2.660E-01	6.830E00	4.082E-22	-2.357E-00
H2O + H2 Q(01)	1.980E-01	3.937E00	3.755E-16	1.380E-00
H2O + H2 Q(02)	3.950E-01	4.387E00	1.630E-16	1.734E-00
H2O + H2 Q(03)	4.410E-01	2.628E00	2.205E-18	-3.184E-01
H2O + H2 Q(04)	4.650E-01	3.488E00	1.183E-18	4.102E-01
H2O + H2 Q(12)	1.980E-01	2.398E00	1.939E-16	7.175E-01
H2O + H2 Q(13)	2.430E-01	4.588E00	5.263E-17	1.374E-00
H2O + H2 Q(14)	2.680E-01	5.631E00	2.619E-17	1.999E-00
H2O + H2 Q(23)	4.560E-02	3.992E00	5.143E-18	3.068E-01
H2O + H2 Q(24)	7.000E-02	4.180E00	3.589E-18	5.583E-01
H2O + H2 Q(34)	2.440E-02	9.229E00	5.393E-18	2.230E-00
H2O + H2O Q(01)	1.980E-01	5.160E00	2.754E-17	1.287E-00
H2O + H2O Q(02)	3.950E-01	3.355E00	8.759E-19	-3.844E-01
H2O + H2O Q(03)	4.410E-01	3.260E00	5.112E-20	1.400E-00
H2O + H2O Q(04)	4.650E-01	3.134E00	2.065E-20	1.100E-00
H2O + H2O Q(12)	1.980E-01	3.682E01	1.676E-18	-1.709E-00
H2O + H2O Q(13)	2.430E-01	3.977E00	2.756E-17	1.144E-00
H2O + H2O Q(14)	2.680E-01	3.728E00	5.328E-18	9.232E-01
H2O + H2O Q(23)	4.560E-02	6.307E00	1.993E-16	2.017E-00
H2O + H2O Q(24)	7.000E-02	5.153E00	1.067E-16	1.835E-00
H2O + H2O Q(34)	2.440E-02	1.157E00	1.419E-16	2.017E-01
H2O + CO2 Q(01)	1.980E-01	1.098E01	1.708E-19	1.569E-00
H2O + CO2 Q(02)	3.950E-01	8.663E00	9.932E-21	6.524E-02
H2O + CO2 Q(03)	4.410E-01	1.481E01	1.103E-19	4.090E-00
H2O + CO2 Q(04)	4.650E-01	5.116E00	1.689E-23	3.680E-00
H2O + CO2 Q(12)	1.980E-01	4.923E00	3.386E-19	3.393E-01
H2O + CO2 Q(13)	2.430E-01	2.119E01	1.793E-16	8.457E-00
H2O + CO2 Q(14)	2.680E-01	1.451E01	9.282E-18	5.192E-00
H2O + CO2 Q(23)	4.560E-02	8.291E00	2.392E-17	1.948E-00
H2O + CO2 Q(24)	7.000E-02	7.518E00	5.091E-17	2.180E-00
H2O + CO2 Q(34)	2.440E-02	4.117E00	1.289E-16	9.704E-01
CO2 + H2 Q(01)	8.280E-02	3.748E00	4.420E-16	1.244E-00
CO2 + H2 Q(02)	1.660E-01	2.133E00	1.142E-16	3.772E-01
CO2 + H2 Q(03)	1.640E-01	4.145E00	9.133E-17	1.176E-00
CO2 + H2 Q(04)	2.910E-01	5.473E00	2.600E-17	1.721E-00

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Table con't.

| REACTION	ET (ev)	C2	C3	C4
CO2 + H2 Q(12)	8.280E-02	2.267E00	8.757E-16	9.479E-01
CO2 + H2 Q(13)	8.090E-02	1.395E00	2.359E-17	4.906E-02
CO2 + H2 Q(14)	2.090E-01	3.476E00	5.288E-18	4.379E-01
CO2 + H2 Q(32)	2.000E-03	5.107E01	8.254E-38	7.115E-00
CO2 + H2 Q(24)	1.260E-01	7.104E00	9.580E-18	1.683E-00
CO2 + H2 Q(34)	1.280E-01	4.391E00	5.831E-18	3.820E-01
CO2 + H2O Q(01)	8.280E-02	4.693E00	1.256E-16	1.173E-00
CO2 + H2O Q(02)	1.660E-01	5.237E00	2.408E-17	1.217E-00
CO2 + H2O Q(03)	1.640E-01	4.624E00	1.387E-18	2.679E-01
CO2 + H2O Q(04)	2.910E-01	4.696E00	1.870E-20	-1.638E-00
CO2 + H2O Q(12)	8.280E-02	6.947E00	5.245E-17	1.795E-00
CO2 + H2O Q(13)	8.090E-02	6.495E00	8.598E-18	1.726E-00
CO2 + H2O Q(14)	2.090E-01	1.164E01	7.792E-16	5.282E-00
CO2 + H2O Q(32)	2.000E-03	1.030E01	6.608E-21	1.440E-00
CO2 + H2O Q(24)	1.260E-01	1.488E01	1.483E-15	6.078E-00
CO2 + H2O Q(34)	1.280E-01	4.601E00	9.341E-19	-4.290E-01
CO2 + CO2 Q(01)	8.280E-02	1.955E01	4.993E-19	4.957E-00
CO2 + CO2 Q(02)	1.660E-01	1.144E01	3.059E-20	1.324E-00
CO2 + CO2 Q(03)	1.640E-01	1.630E01	4.223E-20	3.693E-00
CO2 + CO2 Q(04)	2.910E-01	1.926E01	1.209E-17	7.240E-00
CO2 + CO2 Q(12)	8.280E-02	2.804E00	4.183E-18	0.0
CO2 + CO2 Q(13)	8.090E-02	1.064E01	2.919E-19	2.411E-00
CO2 + CO2 Q(14)	2.090E-01	2.067E01	1.880E-15	8.969E-00
CO2 + CO2 Q(32)	2.000E-03	1.048E00	2.062E-17	0.0
CO2 + CO2 Q(24)	1.260E-01	1.968E01	7.164E-16	7.333E-00
CO2 + CO2 Q(34)	1.280E-01	8.858E00	6.543E-20	2.766E-01
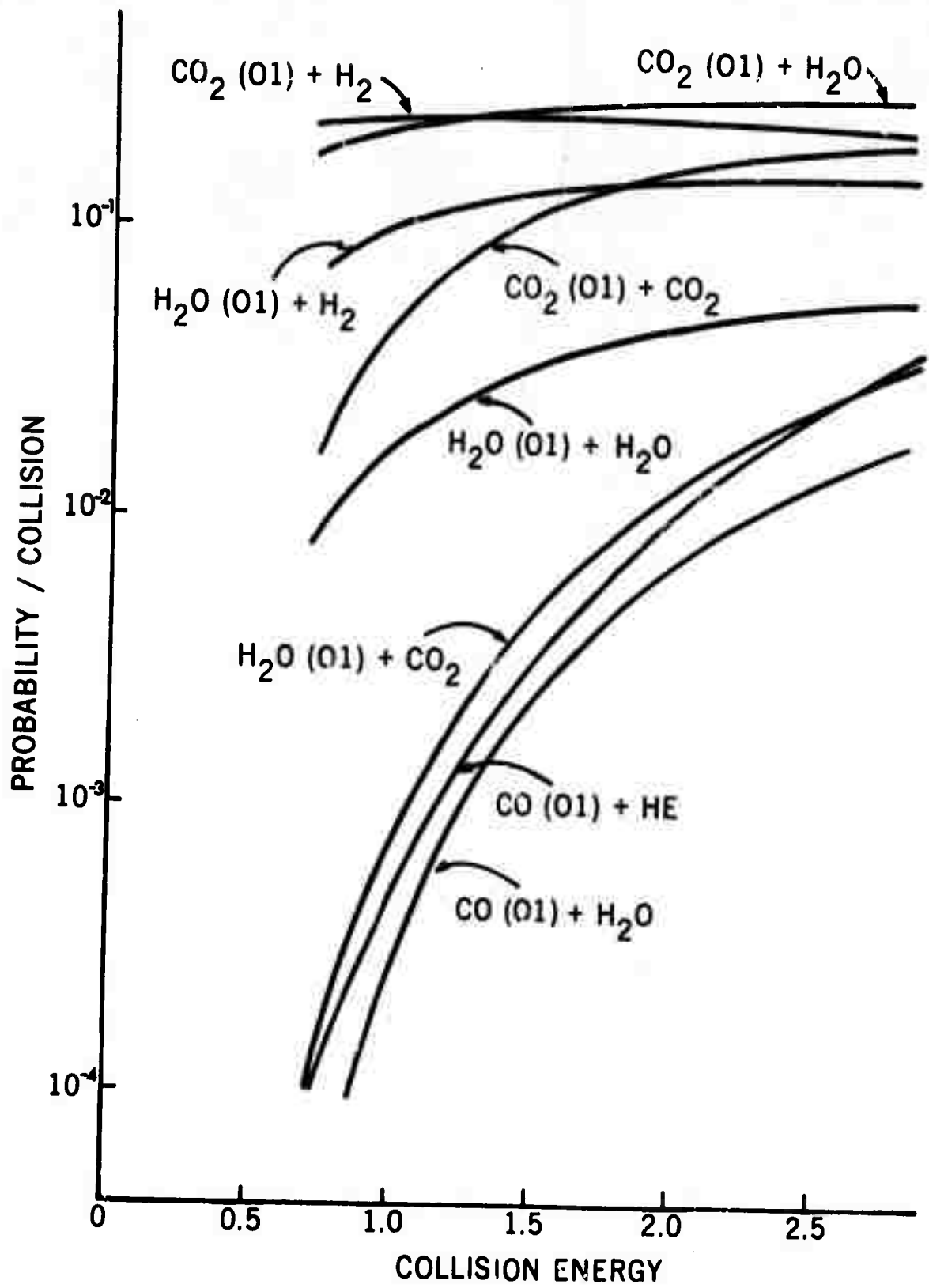
Figure 1: Vibrational excitation probabilities per collision
as a function of collision energy.

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III. Results

CO(v) + He[7]

The relaxation time measurements of Millikan[12] serve as a comparison of the cross section data shown in Table III. The temperature dependence of the calculated relaxation time as derived from the cross sections is in good agreement with the experimental value f $\cdot$ all temperatures above about 300 K and follows a $T^{-1/3}$ dependence in accordance with the Landau-Teller theory[9]. The magnitude of the relaxation times is about a factor of 3 lower than experiment indicating that the cross sections may be large by about the same amount.

This rather good agreement with experimental values was obtained after the use of experimentally measured interaction potential data[13,14] as opposed to the Lennard-Jones or Stockmeyer form used throughout most of the other calculations presented here. The Lennard-Jones results[7] gave relaxation times about 50 times faster than experiment, suggesting that the steeply repulsive r^{-12} behavior at short range is too repulsive. The improvement by using the more weakly repulsive beam data reflects the observed fact that the repulsive potential for atoms interacting with molecules is usually considerably weaker than r^{-12} (more like r^{-7} or r^{-8})[15].

CO(v) + H$_2$O[8]

Figure 2 shows the comparison between the calculated relaxation times from the cross section data and available experimental data[16,17]. The most recent data of von Rosenberg, Bray and Pratt[16] obtained at shock tube temperatures appears to be the most reliable. Clearly a large discrepancy exists between the calculated and measured results particularly at low temperatures. This difference is undoubtedly due, at least in part, to the neglect of VR and VV processes in calculating
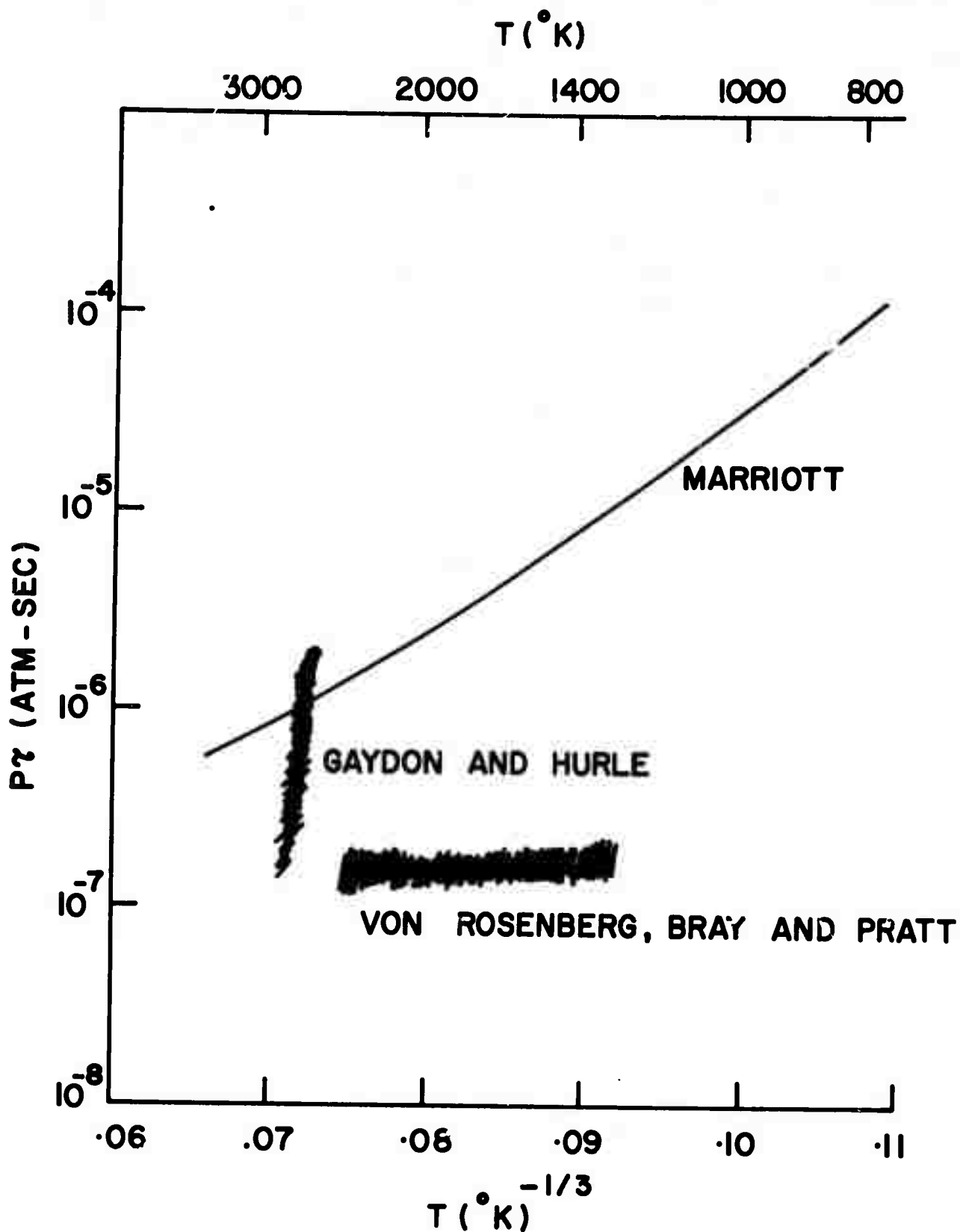
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Figure 2: Comparison between the calculated relaxation time
and available measurements for the $CO(\nu_2) + H_2O$
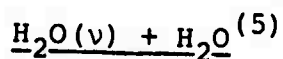energy transfer reaction.

the relaxation times. Inclusion of these processes would tend to preferentially decrease the lower temperature relaxation times and provide a better agreement with data. It is important to note that the extrapolated high temperature relaxation values are in fairly good agreement with the extrapolated data. At high temperatures (above about $400^{\circ}-5000\ ^{\circ}K$), VT contributions become relatively more important, therefore, the cross section results outlined in this report are expected to provide a more accurate description of the excitation process for relative collision energies above about 0.5 ev.

$H_2O(\nu)\ +\ H_2$ (5)
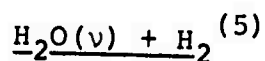
There is no experimental data on the relaxation of H_2O by H_2 so only inferences can be made on the reliability of the cross section calculations. Certainly at low temperatures (below about 2000 K) calculated rate coefficients from the cross section data are likely to be low (relaxation times slow) due to the neglect of VR processes. Since both H_2 and H_2O have low moments of inertia, VR processes are likely to dominate the thermal relaxation process[18]. At higher temperatures, VT processes become relatively more important and the cross section data should become more reliable.

Also based on the $CO_2(\nu_2)\ +\ H_2O\ (H_2)$ relaxation times to be presented later in this section, the high temperature calculation of $H_2O(\nu_2)\ +\ H_2$ is expected to be pretty good. The argument for this expected agreement is somewhat obtuse and assumes that the major contribution to agreement with experimental results comes from the form of the interaction potential. The argument is based on the observation that the calculated $CO_2(\nu_2)\ +\ H_2O$ high temperature relaxation times are in good agreement with data while the $CO_2\ (\nu_2)\ +\ H_2$ relaxation times are about an order of magnitude faster than data support (vida infra). By contrast, the relaxation times are about an order of magnitude too slow. Therefore, since the inter-action of H_2 and H_2O with CO_2 and H_2O are expected to be

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somewhat similar, the noted discrepancies in the CO_2 and H_2O relaxation results would be expected to cancel and thus the $H_2O(\nu_2)$ + H_2 results should be moderately good. The expected reliability should be better at higher temperatures where VT processes are expected to be important in the relaxation process, although the degeneracy in the ν_2 mode of CO_2 and the close resonance existing between the $2\nu_2$ mode and the ν_1 mode of CO_2 somewhat weaken this agreement.

$\underline{H_2O(\nu) + H_2O}$ (5)

The relaxation of $H_2O(\nu_2)$ by H_2O is another energy transfer process in which the low temperature relaxation behavior is likely to be dominated by VR and VV processes. The calculated VT relaxation times should be considerably longer than experimental values[19-20]. This discrepancy is clearly shown in Figure 3. As in the earlier comparisons of this section, the agreement becomes considerably better at high temperatures where VT processes become more important.

Unfortunately due to the extremely fast relaxation times found for H_2O, high temperature data has not yet been obtained. Based on a simple extrapolation of the low temperature data, the predicted relaxation times are about an order of magnitude too slow. This implies that the cross sections are about an order of magnitude too small. Until additional experimental data become available, a more reliable assessment of the calculated cross sections cannot be made.

$\underline{H_2O(\nu) + CO_2}$ (8)
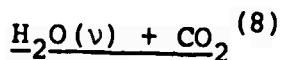
There is no experimental data available on this relaxation process but some qualitative arguments can be made based on the reverse relaxation process, i.e., $CO_2(\nu_2)$ + H_2O, for which data exists. As will be shortly demonstrated, the calculated $CO_2(\nu_2)$ + H_2O high temperature relaxation times are in good agreement with experiment. This implies that the interaction potential data used in the calculations is pretty good. Since the same interaction potential is used in the $H_2O(\nu_2)$ + CO_2 relaxation
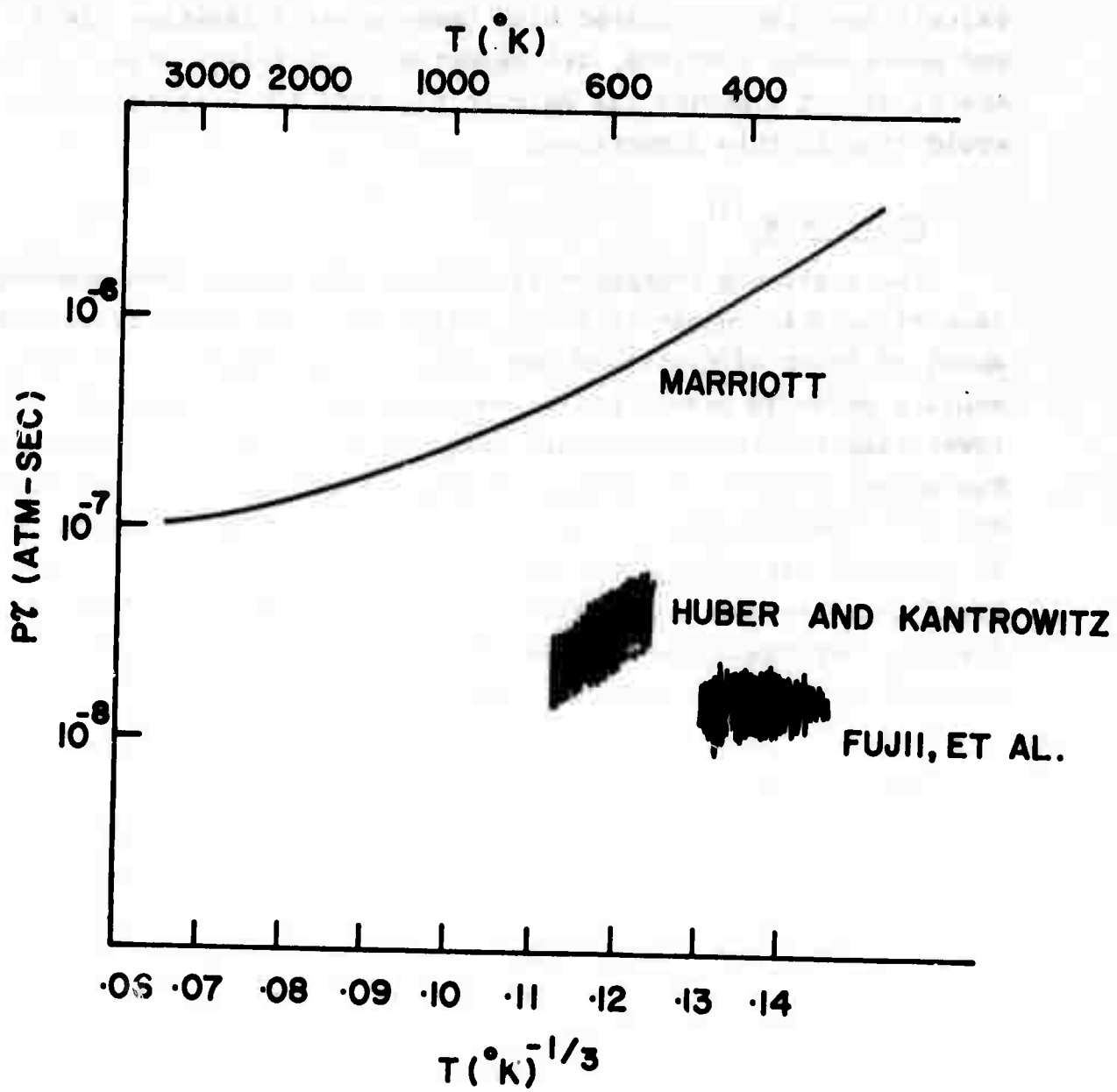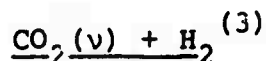
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Figure 3: Comparison between the calculated relaxation time and available measurements for the $H_2O(\nu_2) + H_2O$ energy transfer reaction.

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calculation, the calculated high temperature relaxation times, and hence cross sections, are expected to be fairly good. Again, direct experimental data in the high temperature region would clarify this comparison.

$CO_2(\nu) + H_2$ [3]

The available experimental data on this relaxation process[21,22] (see Figure 4) suggest that the calculated relaxation times are about an order of magnitude too fast. This result is not easy to explain since VR processes are expected to be important at lower temperatures which would make the disagreement even greater. The major factor in this disagreement appears to come from using the r^{-12} Lennard-Jones repulsive potential in this calculation. If a weaker repulsive force law were used, the relaxation times would increase and better agreement would result. Thus, from this limited comparison the calculated cross sections should be reduced by about an order of magnitude.
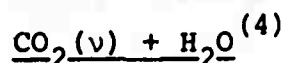
$CO_2(\nu) + H_2O$ [4]

Figure 5 shows the available experimental data on the $CO_2(\nu_2) + H_2O$ reaction[23-26] in comparison to the VT relaxation calculations of Marriott. Again VR processes involving H_2O are likely to reduce the low temperature relaxation time calculations of Marriott bringing better agreement with data below about 1000 K. The high temperature calculated relaxation times appear to agree with the extrapolated data of Shields and Burke[23] and with Lewis and Lee[26] but lie below that of Bulthius and Ponsen[24]. Thus, the high temperature calculations appear to be fairly good for this system. The cross section calculations are therefore expected to be fairly reliable for this energy transfer reaction. It is worth noting that Bulthuis and Ponsen[24] show a comparison of their data with rate coefficients calculated from Marriott's cross sections. Their calculation based on Marriott's cross sections assume a linear interpolation between
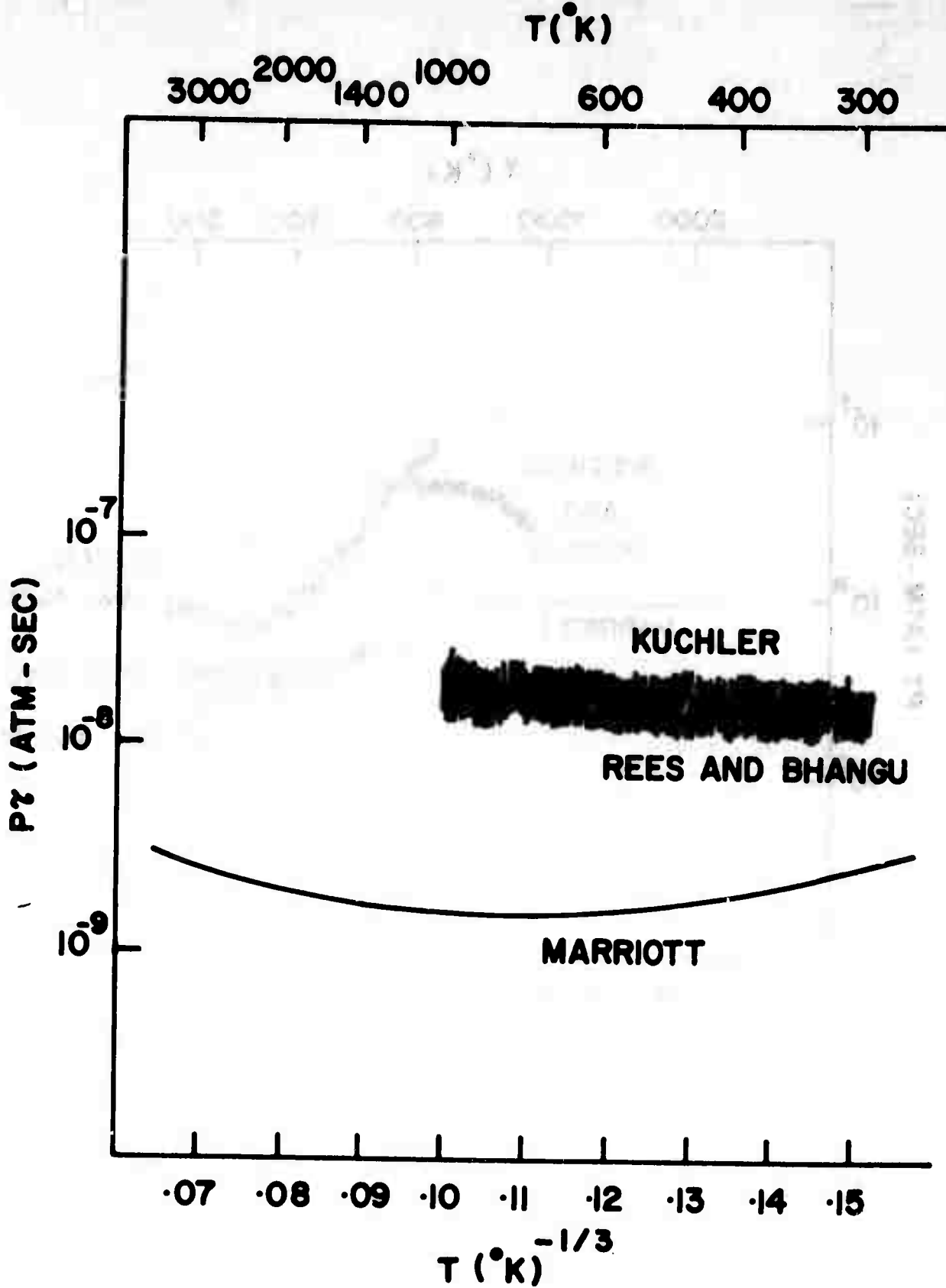
Figure 4: Comparison between the calculated relaxation time and available measurements for the $CO_2(\nu_2)$ + H_2 energy transfer reaction.
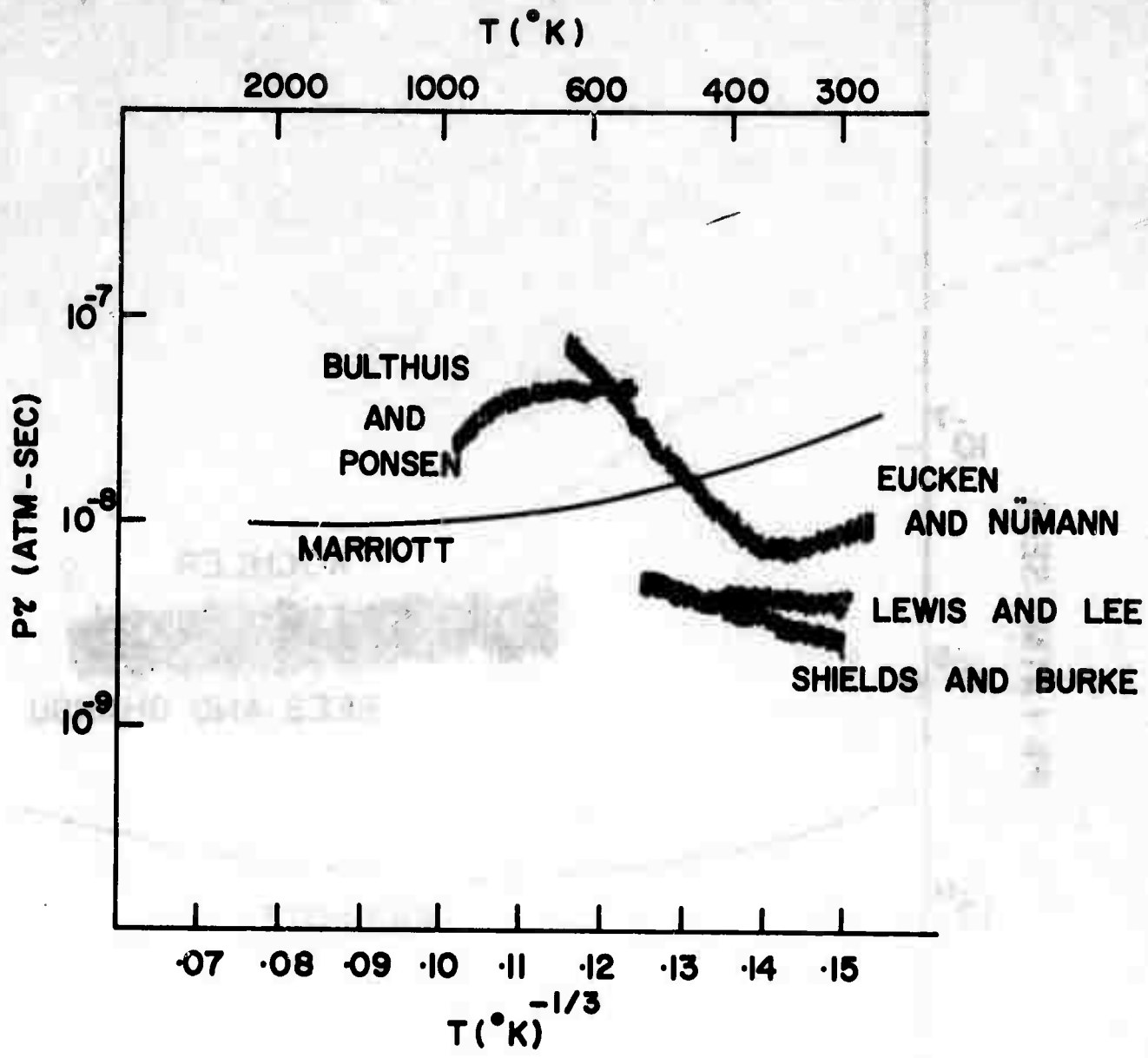
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Figure 5: Comparison between the calculated relaxation time and available measurements for the $CO_2(\nu_2) + H_2O$ energy transfer reaction.

energy-cross section points. The formulation used in this
report to correlate the calculated cross section data is expected
to be considerably better than a linear interpolation, even
though the rate coefficients calculated from this cross section
function give slightly poorer agreement with the data of
Bulthuis and Ponsen.

$CO_2(\nu) + CO_2$ (2)
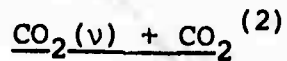
A large amount of experimental relaxation time data is
available on the $CO_2(\nu_2) + CO_2$ relaxation process and is reviewed in
article by Taylor and Bitterman[27]. Figure 6 summarizes this
data and shows the comparison to the calculated relaxation
times of Marriott. Although the calculated temperature dependence
is somewhat stronger than given by the data, the magnitude of
the agreement is pretty good. In the high temperature region
the calculated relaxation times appear too fast by about a
factor of 3. Thus, the cross section data should be reduced by
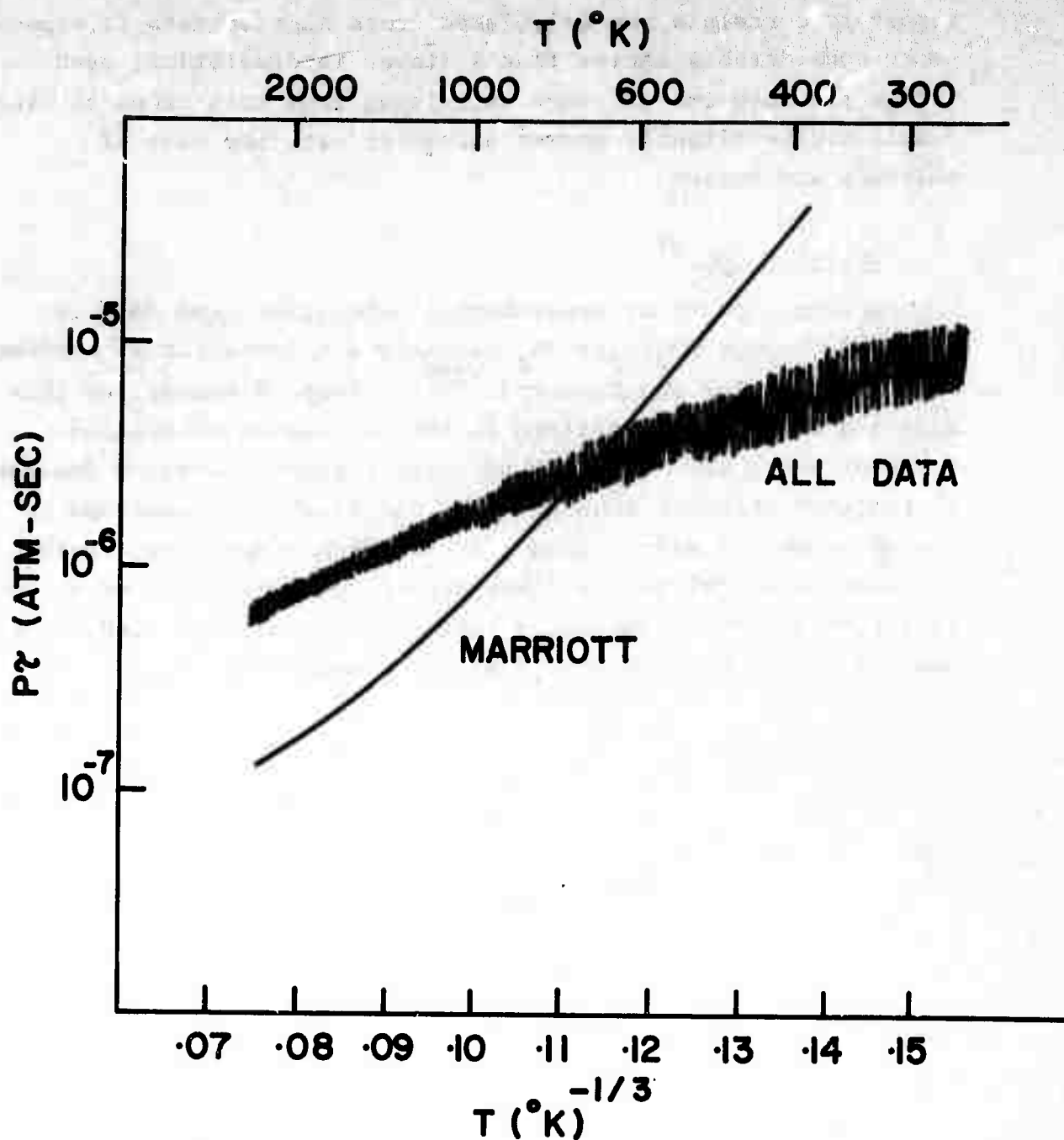about a factor of 3 above 0.5 eV for consistency.

Figure 6: Comparison between the calculated relaxation time and available measurements for the $CO_2(\nu_2) + CO_2$ energy transfer reactions.

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Discussion and Summary

In the preceeding section, relaxation times predicted from the calculated VT cross sections are compared to available relaxation data. This comparison is only made since no direct cross sections have been measured for any of the processes presented in this report. Although on-going experiments at Cornell Aeronautical Laboratories may provide valuable information on the magnitude of some of the excitation cross sections considered in this report. The cross section values presented in this report have all been predicted using a close coupling code based on a structureless particle incident on a spherically averaged molecule. Except for the CO + He calculation, the inter-molecular potential information has been estimated from Lennard-Jones or Stockmeyer potential information. The parameters for these semi-empirical potentials are, in general, determined from transport coefficients[10]. Thus, the potential parameters so determined are sensitive to a different collision energy range than is of interest in the cross section calculations.

In addition, no direct information is input to the code on the shape of the repulsive intramolecular potential for the polyatomic molecules. The classical turning point argument used by Marriott and earlier by Herzfeld and Litovitz[9], appears to be the only method currently available for computing the effect of different collision partners on the form of the intramolecular potential. Current studies are aimed at either clarifying this procedure or suggesting a new methodology for relating intermolecular potential data to the internal coordinates of the molecule.

As pointed out in the theory section, the interaction is modeled by a spherically averaged potential weighted by the method of Keesom[28] for preferential collision directions. For applications where relative collision energies are large (greater than a few eV) while rotational motion is characterized by low temperatures. i.e. effectively a molecular beam configuration, this potential averaging procedure should be replaced by calculating cross sections for different collision angles then averaging the resulting angle dependent cross sections. For the collision systems of concern in

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this report and for collision energies above a few ev's, it is not anticipated that strong angular dependent interactions are dominant, but further studies into this point are underway. It should be noted, however, that the largest quenching cross sections are invariably obtained for non-zero impact parameters. Yet it is only for zero impact parameter that a fixed orientation can normally be maintained during a collision. Therefore, some type of potential averaging procedure will always be the most realistic approximation to the scattering potential.

In general, the agreement obtained between high temperature rate data and the calculated relaxation times is rather good. Although indirect, this agreement tends to support the hypothesis that the calculated VT cross sections given in Table III are the most reliable source of excitation data at the present time for use in the chemical modeling of rarefied plume environments.

Current studies are addressing some of the approximations used in the codes and in obtaining O atom scattering data for use in calculating the vibrational excitation cross sections for plume species by atmospheric O atoms.

A complete tabulation of the calculated vibrational excitation rate coefficients over the temperature range 300 to 5000 K is available by writing directly to the author. Although these calculated rate coefficients provide the only source of information on excitation processes involving other than the v_2 mode of CO_2 and H_2O, the predicted values are subject to considerable uncertainty due to the neglect of both VR and VV processes. Further, scaling of the higher order excitation rate coefficients by the discrepancy found in the v_2 relaxation time comparisons may be considerably in error but this procedure may at least lead to order of magnitude estimates.

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