LOW-ENERGY MOLECULAR COLLISION PROCESSES IN SPACE

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ABSTRACT. Among the low-energy nonreactive molecular collisions, the rotational and vibrational transitions are the most important inelastic processes. The collision partner is an electron, an ion, or a neutral particle. Depending on the process and the collision system concerned, the magnitude and the energy dependence of the relevant cross sections are widely different. The present status of our knowledge is briefly summarized and some sample cross section data for H_2 and CO are shown. Useful relations among the rotational cross sections are indicated. The importance of the long-range intermolecular forces in determining some chemical reaction rates is also pointed out.

1. INTRODUCTION

Collision processes involving molecules play important roles in cooling, heating, and determining chemical composition of gases in stellar, circumstellar, planetary and cometary atmospheres and in interstellar medium. Types of relevant collision processes are (A, B, C are atoms or molecules; processes involving grains are excluded):

I. Molecular formation
$A + B \rightarrow AB + h\nu$; $A^- + B \rightarrow AB + e$;
$A^* + B \rightarrow AB^+ + e$; $A + B + C \rightarrow AB + C$, etc.
II. Molecular destruction
$AB + h\nu \rightarrow A + B$; $AB + e \rightarrow A + B + e$ (or $\rightarrow A^- + B$);
$AB^+ + e \rightarrow A + B$; $AB + C(\text{excited}) \rightarrow A + B + C$;
$AB + C(\text{or } C^+)(\text{fast}) \rightarrow A + B + C(\text{or } C^+)$;
$AB + He^+(\text{slow}) \rightarrow A + B^+ + He$, etc.
III. Rotational and vibrational transitions
$AB + C(\text{or } C^+ \text{ or } e) \leftrightarrow AB\dagger + C(\text{or } C^+ \text{ or } e)$
IV. Charge transfer
V. Chemical reaction

The atom interchange reaction $H + H_2 \rightarrow H_2 + H$ is important since it makes the para-ortho conversion of H_2 possible at higher temperatures This reaction contributes also to the rotational and vibrational transi-

M. S. Vardya and S. P. Tarafdar (eds.), Astrochemistry, 31–41.

tions in H_2. (Blais and Truhlar, 1981) As the temperature goes down, the probability of this process becomes very small. Then $H^+ + H_2$ collision becomes more important in the para-ortho conversion of H_2. (Dalgarno, et al. 1973) The influence of the long-range forces at low-temperature reactive collisions will be discussed briefly at the end of this review.

2. ROTATIONAL AND VIBRATIONAL TRANSITIONS

2.1. Experimental Studies

Some of the frequently used experimental methods include (i) anomalous dispersion and absorption of ultrasonic waves, (ii) structure of shock waves, (iii) time-resolved photoacoustic detection method, (iv) various double or triple resonance methods, (v) laser-induced fluorescence, and (vi) molecular beam experiments. In (i)-(v), usually, one of or both molecules in collision are distributed in various excited states and in different translational motion. Unless a single process is known to be dominant, it is often difficult to analyse data and derive uniquely the probabilities of individual collision processes. Beam experiments, in principle, give us possibility of specifying the internal states of the two colliding molecules and the relative velocity before and after the collision. [Reviews on beam experiments: Toennies (1976), Faubel (1983)] So far, however, the integrated (over angles) cross section of an inelastic process as a function of the collision energy has been seldom reported.

Experimental data are useful as they provide tests to various theoretical calculations. Collaboration between theory and experiment is most useful to derive accurate cross sections.

2.2. Theoretical Studies

In studying molecular collisions theoretically, we must have detailed knowledge of the intermolecular forces and method of handling the dynamical problems. When I studied the rotational and vibrational transitions in molecular collision thirty years ago, accurate intermolecular potentials were not yet available. Furthermore, the electronic computer was still in its infancy and naturally the results were not very accurate. Since then, the rapid development of computer technique stimulated the progress in computational physics and efficient approaches were proposed to solve a big set of coupled differential equations which characterized the collision theory. In 1970's, the standard close-coupling method, the somewhat simpler coupled-state method, the infinite-order sudden (IOS) approximation (appropriate to fast collisions), the classical trajectory calculations and some other approximation methods were applied to various molecular collision processes. Range of applicability of each method has been more or less established.

As to the intermolecular interactions, early studies mostly used semiempirical analytic expressions for the relevant potentials. It has

been found soon that different choices of the interaction often give a large difference between the results obtained. In recent years, detailed ab initio calculations of potential energy surfaces have been published for some collision systems and using these fairly accurate potentials the dynamical problems have been solved to obtain cross sections. Although the accurate potential calculation is not an easy task, more efforts along this line should be encouraged.

2.3. Rotational and Vibrational Transitions in H_2 and CO

In Fig. 1 the elastic and rotational cross sections are shown for collisions of H_2 with H, He or another H_2. These are results of various theoretical calculations. Discrepancies within the same collision system is largely due to the different interaction potentials chosen by different authors.

In Fig. 2 the vibrational de-excitation cross section is shown for the collision with He or another H_2. Here again, different potentials chosen give significantly different cross sections. The excitation cross section for v=0 → 1 (threshold ≅ 0.5eV) can be obtained from the de-excitation cross section by the well-known relation of detailed balance.

In Fig. 2, the de-excitation cross sections for CO are also shown. It is seen that H_2 is considerably more efficient than He to de-excite the vibration of CO. [The calculation for He was not to compare with experimental results, so that the magnitude of this cross section in Fig. 2 should not be taken too seriously.]

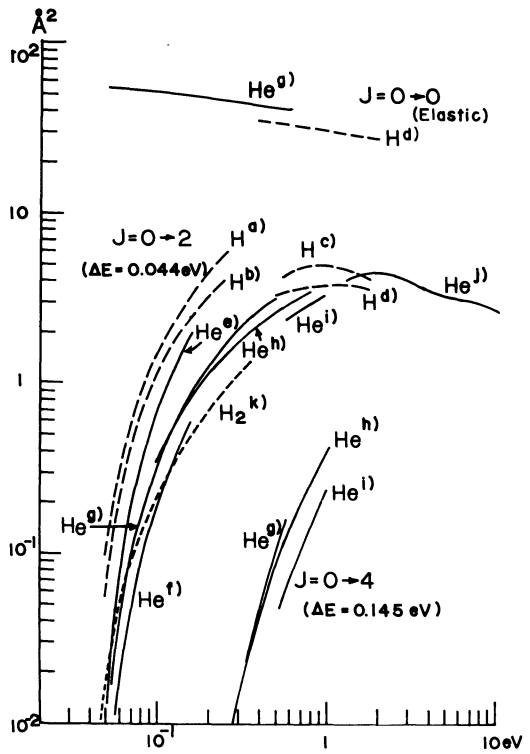

Figure 1. Elastic and rotational excitation cross sections (J=0 → 0,2,4) of H_2. Each line is labelled with respective collision partner (H, He or H_2).

[References: a)Dalgarno et al. (1966); b)Allison & Dalgarno (1967); c)Chu & Dalgarno (1975); d)McGuire & Krüger (1975); e)f) Johnson & Secrest (1968); g) Eastes & Secrest (1972); h) Billing (1978); i)Gerratt & Wilson (1980); j)Dove et al. (1980)]

https://doi.org/10.1017/S0074180900153756 Published online by Cambridge University Press

It is interesting to see also that the rotating H_2 is more efficient than the nonrotating H_2. A similar difference between the rotating and nonrotating H_2 is noticed also in the rotational cross sections of CO (Fig. 3). In the temperature range relevant to the interstellar molecular clouds (T < 100K), the ortho-H_2(J=1) is considerably more efficient than the para-H_2(J=0) in exciting the rotation of CO.

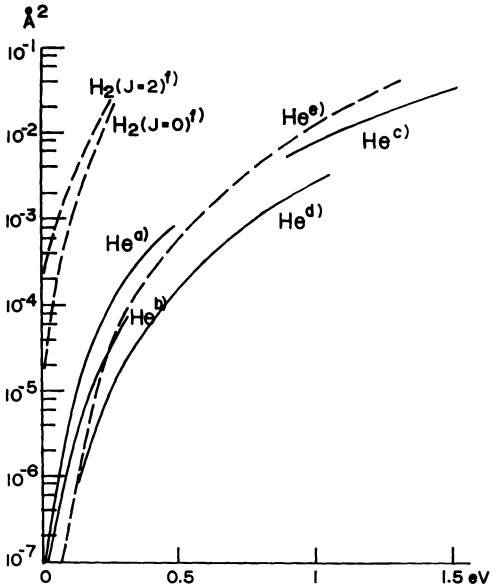

Figure 2. Rotationally-summed vibrational de-excitation (v = 1 → 0) cross sections of H_2 and CO from the state v=1, J=0 as functions of the initial energy E_{cm}. Solid lines are for H_2; dashed lines for CO. Each line is labelled with respective collision partner (He or H_2).

[References: a)Alexander & McGuire (1976); b)Billing (1978); c)Raczkowski et al.(1978); d)Orlikowski (1981); e) Price et al. (1983); f) Bačić et al.(1985)]

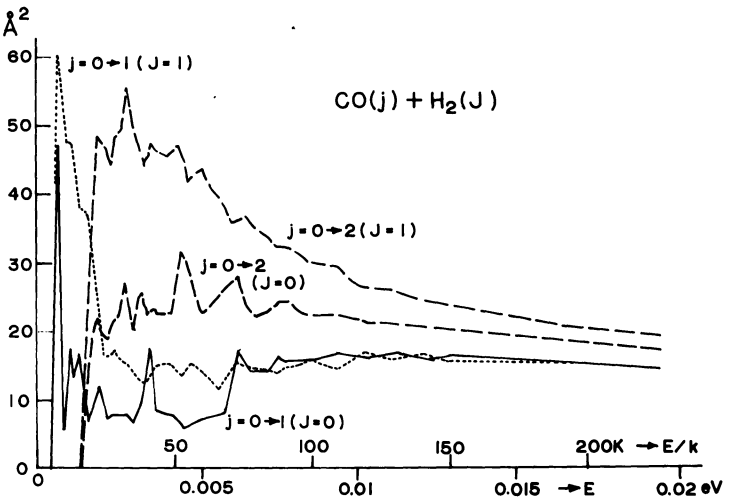

Figure 3. Rotational excitation of CO in collision with H_2(J=0 or 1). Cross sections are shown as functions of the collision energy E_{cm}. [Reference: Brechignac et al.(1980)]

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The rotational cross section for H_2: J=0 → 2(Fig.1) has a maximum at about 1 eV, while the cross sections for CO: J=0 → 1,2 have sharp peaks just above the respective threshold. This difference can be understood, at least qualitatively, by the Massey's criterion. The Massey parameter is defined by [see, e.g., Nikitin (1974)]

$$w = a\,\Delta E/\hbar v, \qquad (1)$$

where a is the range of the relevant interaction, ΔE is the energy transfer between the translation and the internal degrees of freedom, $2\pi\hbar = h$ is the Planck's constant and v is the velocity of relative motion. The criterion says that "if $w \gg 1$, the cross section for the inelastic collision under consideration should be negligibly small". Very often the cross section maximum comes in the velocity region where $w \sim 1$. By comparing the collision energy $E = E_m$ corresponding to $w = 1$ and the threshold energy, one can infer whether the maximum is just above the threshold or far above the threshold.

Rotational transitions of CO in collision with He has been studied by Green and Thaddeus (1976) and by Thomas et al.(1980). The cross sections for J=0 → 1 obtained in these two calculations are not much different from each other. The cross section has sharp peaks (30-40 $Å^2$) just above the threshold and decreases rather rapidly as energy increases. For J=0 → 2, however, there is a large discrepancy between the two calculations due to the different potentials adopted.

Let us now turn to the rotational and vibrational transitions of H_2 and CO induced by electron or proton. The rotational cross section of H_2 has been obtained experimentally by Crompton et al.(1969)(electron swarm experiment) and by Linder and Schmidt (1971)(beam experiment). For proton impact, available data are fragmentary. [McGuire (1976); Schinke et al.(1980)]

For vibrational excitation v = 0 → 1 by electron, Linder and Schmidt (1971) and more recently Nishimura et al.(1985) have measured the cross section. For proton collisions, Herrero and Doering (1972) measured the cross section. Below about E_{cm} = 100 eV, the values obtained are lower bounds of the cross section, but at higher energies, the results are supposed to be more accurate. Theoretical calculations [Schinke (1977), Schinke et al.(1980)] give cross section much larger than the experimental values.

For electron-CO collisions, the rotational excitations have been calculated by Chandra (1977) and by Saha et al.(1981). The most remarkable feature of the results is that the cross section for J=0 → 1 becomes very large at low collision energies ($\sim 10^2$ $Å^2$ at $E \sim 1$ meV). This is due to the long-range dipole interaction. Similarly, a large cross section is found for proton impact (Sakimoto, 1983). At E_{cm} = 20 meV, cross section has a maximum of more than 2500 $Å^2$. It is a surprise to see that such a large cross section is produced by a small dipole moment of CO. Generally, in rotational transitions in ion-polar molecule collisions, the dipole interaction is dominant and the main contribution to the cross section comes from distant encounters. Therefore, the relative motion does not deviate much from the straight trajectory, classically speaking. Under these circumstances, it can be shown

(Takayanagi, 1978) that the reduced cross section $\sigma/(DZe/B)$, which is a dimensionless quantity, is a function of the reduced velocity $\beta = \hbar v/\sqrt{(DZeB)}$, where σ is the rotational cross section, D and B are the dipole moment and the rotational constant (in energy unit) of the polar molecule, and Ze is the ionic charge.

The large difference in the location of the CO cross section maximum for proton-, electron-, and He-collisions can be understood again in terms of the Massey's criterion.

The vibrational excitation v=0 → 1 of CO by electron was studied by Ehrhardt et al.(1968). The cross section has a very large contribution of a shape resonance in the 1 ∿ 3 eV region where the probability of excitation to higher vibrational states is also large. More recently, Sohn et al.(1985) studied the near-threshold region, while Chutjian and Tanaka (1980) studied the energy region above the resonance. Data from electron swarm experiments have been analyzed by Land (1978). Gianturco et al.(1980) have studied proton-induced vibrational excitation of CO.

2.4. Scaling Laws (Relation among the Cross Sections)

The scaling law for the rotational cross section in the ion-polar molecule collision has been mentioned in §2.3. Using this relation, the theoretical or experimental cross section can be easily transferred from one system to other systems. Similarly, if the target molecule is nonpolar and has a large quadrupole moment Q, it can be shown (Takayanagi, 1982) that the reduced rotational cross section $\sigma(J\to J')/(|QZ|e/B)^{2/3}$ is a function of the reduced velocity $\beta' = \hbar v/(|QZ|eB^2)^{1/3}$. In this case, the cross sections depend considerably on the sign of QZ. For vibrational transitions, ΔE is much larger, so that various short-range interactions become important as the Massey's criterion tells us. Thus there is no simple scaling law of the kind mentioned above.

In most theoretical works on rotational transitions, the excitations from the ground level (J=0) are studied. In astronomical applications, however, the cross sections for transitions between excited levels are often required. Fortunately, when the collision velocity is not too low and the collision duration is short, so that the molecular orientation can be regarded fixed during collision ("sudden" approximation), there holds a very simple relation between the σ's:

$$\sigma(J\to J';E) = \sqrt{(E'/E)}\cdot\sum_{J_t=|J-J'|}^{J+J'} [C(JJ_tJ';000)]^2\ \sigma(0\to J_t;E), \quad (2)$$

where E and E' are the energies of relative motion before and after the collision ($E'/E \cong 1$ when the sudden approximation is valid), and C(...) is the usual Clebsch-Gordan coefficient. In many cases, $\sigma(0\to J_t)$ becomes small fairly rapidly as J_t increases, so that $\sigma(J\to J';E)$ is determined by a small number of $\sigma(0\to J_t;E)$. In other words, the rotational cross sections and also the rate constants, which are obtained from the cross sections by integration over velocity, can be represented by a small number of parameters. "Fitting laws" of this kind and of other types have been discussed in detail by Brunner and Pritchard (1982).

For electron collisions, the collision velocity is higher so that the sudden approximation holds better here than in heavy particle collisions. Shimamura (1984) discussed relations between the cross sections for electron-molecule collisions.

2.5. Rotational and Vibrational Transitions in Other Molecules

Table I lists some molecules (other than H_2) of astronomical interest for which theoretical calculations have been done on rotational and/or vibrational transitions in collisions with H, He or H_2. The list is probably far from complete. Accuracy of the reported data varies from work to work.

TABLE I. Some references reporting theoretical cross sections or rates. (R;He) means "pure rotational transitions in He-impact", (V) is for vibrational transitions.

HD	[1][2][4][11]	[1] Itikawa & Takayanagi(1972)(R;He); [2] Green (1974)(R;He); [3] Green & Thaddeus(1974)(R;He); [4] Chu(1973)(R;H_2); [5] Green(1975)(R;He); [6] Garrison et al.(1976)(R;He); [7] Green & Thaddeus(1976)(R;H,He); [8] Green(1978)(R;He); [9] Green & Chapman(1978)(R;He,H_2); [10] Green et al.(1978)(R;He); [11] Billing(1980)(V;He); [12] Brechignac et al.(1980)(R;H_2); [13] Green (1980b)(R;He); [14] Green(1980a)(R;He,H_2); [15] Thomas et al.(1980)(R;He); [16] Bieniek & Green(1981)(V;He); [17] Clary(1981)(V;He); [18] Billing & Clary(1982)(V;He); [19] Bieniek & Green(1983)(V;H_2); [20] Dewangan & Flower (1983,1985)(R;H_2); [21] Gianturco et al.(1983) (V;He); [22] Price et al.(1983)(V;He); [23] Monteiro(1984)(R;He); [24] Schinke & Andresen (1984)(fs,Λ;H_2); [25] Bacic et al.(1985)(V;H_2); [26] Billing et al.(1985)(R;He); [27] Billing & Diercksen(1985)(R;H_2); [28] Davis(1985)(R;He) ; [29] Flower & Launay(1985)(R;H_2); [30] Monteiro(1985)(R;H_2); [31] Schinke & Diercksen (1985)(V;He).
CO	[7][8][12][15]	
	[22][25][29][31]	
SiO	[16][19]	
CS, OCS	[9]	
OH	[20][24]	
H_2O	[14]	
CO_2	[17][18][21]	
HCN	[3]	
HCO^+	[23][30]	
HCS^+	[23]	
HC_3N	[9]	
H_2CO	[6][10]	
NH_3	[13][26][27][28]	

3. INFLUENCE OF LONG-RANGE FORCES ON CHEMICAL REACTIONS

Ion-molecule reactions often have large rate constants down to very low temperatures. This is usually explained as due to the polarization interaction. When there is a critical impact parameter $b = b_c$ such that for $b < b_c$ the colliding pair come to a short distance and have a violent collision, while for $b > b_c$ the collision is a distant one, the cross section πb_c^2 is called the "hitting"(or "capture") cross section. For polarization interaction, this is known as the Langevin cross sec-

https://doi.org/10.1017/S0074180900153756 Published online by Cambridge University Press

tion. The rate constant k_L calculated from the Langevin cross section is temperature independent and often has a large value of the order of $10^{-9}cm^3$/molecule•sec. When the molecule has a dopole moment, the long-range dipole interaction affects the collision dynamics. To study such an effect, ADO (Average Dipole Orientation) theory proposed by Su and Bowers (1973) is often applied. This method was later improved by Bates (1982,1983). The PRS (Perturbed Rotational State) approach, which was introduced to study rotational transitions, is more firmly based on the collision theory [Takayanagi(1978)]. It starts with the adiabatically perturbed rotational states. When necessary, transitions among different adiabatic states can be taken into account. This theory has been used to study the modification of the Langevin cross section by the dipole interaction [Sakimoto and Takayanagi(1980); Sakimoto(1984,1985)] and by the quadrupole interaction [Takayanagi(1982)]. In Fig. 4, the hitting rate constants k_o relative to k_L are shown for ion-polar molecule collisions. The PRS calculations for NH_3 and for a hypothetical linear molecule with $\alpha B/D^2 = 1\times10^{-3}$ confirm the empirical scaling formula

$$k_o(T)/k_L = 0.4767X + 0.62 \qquad (3)$$

derived from classical trajectory calculations by Su and Chesnavich (1982). Here, $X = D/\sqrt{(2\alpha\kappa T)}$ and α is the polarizability of the molecule and κ is the Boltzmann constant. The curve labelled "Celli et al." (1980) has been obtained by a statistical approach. In the locked dipole model the dipole orientation is fixed to the direction of the ion.

Clary (1984) has shown that long-range intermolecular interaction affects the chemical reaction rate even in neutral-neutral reactions.

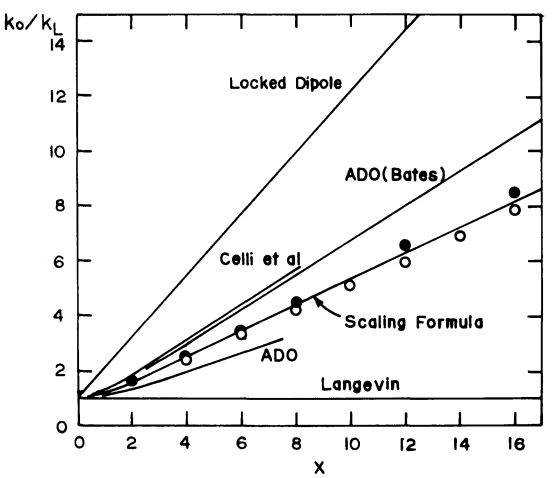

Figure 4. Rate constant ratio k_o/k_L for ion-polar molecule collision vs. $X = D/\sqrt{(2\alpha\kappa T)}$. Filled and open circles are PRS results for a model linear molecule and for NH_3, respectively. These are compared with the scaling formula (3) and other calculations. [This figure has been prepared by Dr.K.Sakimoto.]

Note: For singly-charged ion, $k_L = 2\pi e\sqrt{(\alpha/\mu)}$. e:elementary charge; μ:reduced mass of reacting pair.

ACKNOWLEDGEMENTS. I would like to thank Dr. K.Sakimoto for providing me with Fig. 4 and for assisting me in literature survey.

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DISCUSSION

MITRA: There are no measurements in this energy region with these systems?
TAKAYANAGI: To my knowledge, there are, unfortunately, no experimental data available for the processes of interest. Therefore, we cannot compare our calculations with experiments.

DALGARNO: How does your calculated rate coefficients (Fig. 4) depend on the rotational quantum numbers of the reactants?
TAKAYANAGI: The values reported by Sakimoto have been obtained by averaging over the Boltzmann distribution of the rotational states. However, if we look at individual rotational states, the rate constant is larger for lower rotational states.

P.K. GHOSH: Are there any calculations on electron-impact electronic excitation of molecules where detailed rotational-vibrational states are being considered?
TAKAYANAGI: For some simple molecules like H_2 and CO, there are theoretical calculations of the electronic transitions. Usually this is done for fixed molecular orientation and fixed vibrational coordinates and then the resulting cross section is averaged over the orientation (and over the vibrational coordinates unless the internuclear distances are fixed to a particular configuration throughout calculations). If the "sudden" approximation is valid, one can also calculate the detailed rotational-vibrational transitions taking place simultaneously with the electronic transitions, but I do not remember whether such calculations have been actually done.

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