Submitted to Journal of
Chemical Physics

UCRL-19634
Preprint

c.2

RECEIVED
LAWRENCE
RADIATION LABORATORY

JUN 5 1970

LIBRARY AND
DOCUMENTS SECTION

LINEAR, HARMONIC FORCES MODEL FOR REACTIONS OF Cs ATOMS WITH ALKYL IODIDES

David D. Parrish and Ronald R. Herm

May 1970

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

UCRL-19634
c.2

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LINEAR, HARMONIC FORCES MODEL FOR REACTIONS OF Cs ATOMS WITH ALKYL IODIDES

David D. Parrish and Ronald R. Herm

Inorganic Materials Research Division
Lawrence Radiation Laboratory
and
Department of Chemistry, University of California
Berkeley, California 94720

ABSTRACT

The Cs+ alkyl iodide reaction dynamics are investigated by means of a classical, linear, four-particle model, Cs - I - CH_2 - R where R = H, CH_3, C_2H_5 or C_3H_7, with linear harmonic restoring forces between adjacent particles. The full reaction exothermicity is initially partitioned between potential energy of Cs - I extension and I - CH_2 compression, and the trajectories of the four particles are followed until the I - CH_2 distance reaches a critical extension, at which

point the reaction is assumed to be complete. The model is examined as a function of two parameters, the I - CH_2 force constant, k_2 , and the initial repulsive energy in I - CH_2 compression, P. By varying k_2 , the model spans the spectrum of possible direct-interaction reaction dynamics from the limit of the adiabatic, very-slow CsI - CH_2R separation (low k_2 limit) to the limit of impulsive release of the I - CH_2 compression (high k_2 limit). In contrast to previous calculations, we obtain a good qualitative fit to the experimentally reported product recoil energies if: (1) a relatively high value of k_2 , near the impulsive limit, is used; (2) the potential surface is largely repulsive, with P = 19.0 kcal/mole out of a total 28.7 kcal/mole reaction exothermicity; and (3) both the CsI and the CH_2 - R alkyl radical carry off substantial internal excitations.

A wide variety of detailed experimental features of gas phase bimolecular exchange reactions have been obtained from molecular beam and chemiluminescence studies in the last five or ten years. This rapid growth in our experimental knowledge of these reactions has been paralleled by an increasing number of three-dimensional, exact classical trajectory studies, employing extensive numerical integrations on a digital computer, which have reproduced many of the experimentally observed reaction features. In this way, these classical trajectory studies have already been instrumental in elucidating the important features of the interatomic forces in a number of these reactions and will, no doubt, continue to extend our knowledge of these forces for some time to come. Nevertheless, concomitant with this growing body of exact numerical trajectory calculations, it seems worthwhile to continue to examine simple models of the reaction dynamics in order to (1) provide greater physical insight into the possible range of values assumable by a given reaction feature, (2) possibly attempt to correlate different physical phenomena, as, for example, the energy partition in bimolecular exchange reactions and photodissociation, and (3) provide a starting point for estimates of the magnitude of the interatomic forces which

could serve as input information for the more sophisticated, exact trajectory calculations.

This paper reports on the application of one such model to the explanation of the energy partitioning reported by crossed molecular beam studies of reactions of the series $Cs + I - R' \longrightarrow CsI + R'$, where R' is the methyl, ethyl, n-propyl, or n-butyl radical. The model chosen is a harmonic oscillator model in which the Cs - I - R' complex is constrained to be linear and the forces between any two particles are assumed to vary linearly with displacement from an equilibrium internuclear distance so that the overall motion of the particles may be expressed as a superposition of normal modes of oscillation. This model is certainly not new to the chemical literature and was employed extensively by N. B. Slater to discuss the dynamics of unimolecular decomposition. More recently, it has been applied to the problem of the vibrational excitation of a diatomic molecule by collision with an atom[1] and to the problem of the energy partitioning in reactions of the alkali atoms with the halogen molecules.[2]

The full results of the experimental studies of these reactions have not yet been published although the striking qualitative result[3] is that the CsI is observed to be formed with roughly the same center-of-mass (CM) speed irrespective of the R' group; thus, by energy conservation, the internal excitation of the products must increase as R' is varied from methyl to butyl. Most of the exact trajectory studies refer to the $M + ICH_3$ reaction and so are not relevant to the present investigation, although Raff[4] did report exact three-

dimensional trajectory study comparisons of the K + IC_2H_5 and ICH_3 reactions. In addition, Ottinger[3] has reported exact computer solutions of the energy partitioning in the Cs + methyl, ethyl, n-propyl, and n-butyl iodide reactions for a one-dimensional linear collision; his model treated each CH_2 or CH_3 group as a separate particle and his potential energy of interaction between the particles is more sophisticated than that considered here. Nevertheless, his calculation failed to fit the observed constancy of the CsI product CM speed with changing R' groups. The following application of the harmonic oscillator model to these reactions will (1) show that the observed approximate constancy of the CsI CM speed can be accounted for in the impulsive limit, where the R' - I repulsion is the dominant force in the collision, (2) argue that the model should, in fact, provide fairly reliable estimates of the actual energy partitioning because the observed reaction features are so near the impulsive limit, (3) indicate that one should observe substantial internal excitation in the R' product, with the possible exception of the methyl group, and (4) provide a qualitative indication of the important forces, which should help to provide guidelines for the selection of an appropriate potential energy surface for any future exact trajectory calculations for these reactions.

FORMULATION

The reaction is treated as that of four particles, with R' = CH_2 - R, which are constrained to a linear, one-dimensional collision with the bonds labeled as shown in Figure 1. The particles are given the atomic masses of Cs and I for the first two particles and the sum of the atomic

masses of CH_2 and R for the second two particles, where R is H, CH_3, C_2H_5, or C_3H_7. Thus, this model treats the hydrocarbon radical, CH_2 - R, as a diatomic molecule and so predicts the same behavior for Cs + n-butyl and i-butyl iodide, whereas Cs + i-propyl, s-butyl, and t-butyl iodides are not considered. The potential energy is given in terms of Δ_1, Δ_2, and Δ_3, the displacement of each bond length from its equilibrium value, r_i^e (i.e., $\Delta_i = r_i - r_i^e$), as

$$V(\Delta_1, \Delta_2, \Delta_3) = \tfrac{1}{2} k_1\Delta_1^2 + \tfrac{1}{2} k_2\Delta_2^2 + \tfrac{1}{2} k_3\Delta_3^2, \quad \Delta_2 < 0 \qquad (1)$$

$$= \tfrac{1}{2} k_1\Delta_1^2 \qquad + \tfrac{1}{2} k_3\Delta_3^2, \quad \Delta_2 \geq 0 \ .$$

The force constants k_1 and k_3 are taken as equal to those in a conventional Cs - I and C - C bond respectively, whereas r_1^e and r_3^e do not enter into the calculation; thus, k_1 and k_3 are 5.44×10^4 dynes/cm and 4.33×10^5 dynes/cm respectively. The I - CH_2 force constant k_2 is varied as a parameter of the model.

At the start of the reaction all four particles are stationary, i.e., $\dot{\Delta}_1^{(0)} = \dot{\Delta}_2^{(0)} = \dot{\Delta}_3^{(0)} = 0$. Further, $\Delta_3^{(0)} = 0$, $\Delta_2^{(0)} < 0$ and $\Delta_1^{(0)} > 0$ such that ΔD_0, the difference in CsI and I- CH_2 bond dissociation energies, is equal to $V(\Delta_1^{(0)}, \Delta_2^{(0)}, 0)$. Thus, $V(\Delta_1, \Delta_2, \Delta_3)$ has the correct limit of zero as $\Delta_2 \longrightarrow +\infty$ for $\Delta_1 = \Delta_3 = 0$; however, the limiting behavior for separated reactants ($\Delta_1 \longrightarrow +\infty$) is wrong and this model effectively assumes that the very slowly approaching Cs and I - CH_2 - R feel no force until a critical Δ_1 is reached, whereupon Eg.(1) applies and

reaction is certain to take place. The energy initially present in compression of the I - CH_2 bond, $\frac{1}{2} k_2 \Delta_2^{(0)2} = P$, is referred to as the repulsion and can be easily varied as a second parameter of the model while maintaining the total exothermicity, ΔD_0 , constant by simultaneously changing the value of $\Delta_1^{(0)}$. The exothermicities of all these reactions are approximately the same and were taken as $\Delta D_0 = 28.7$ kcal/mole.[6]

Having fixed these initial conditions, the subsequent classical motion of the system is followed by a normal coordinates analysis; the reaction is assumed to be completed when Δ_2 goes through zero. At this point the products are assumed to stop interacting and the partitioning of the reaction exothermicity is determined by decomposing the instantaneous values of the normal coordinates and their time derivatives into vibrational energy in each of the two product diatomics and relative translational kinetic energy of separation, E'. Figure 1 shows an effective potential energy surface for a k_2 value which is found to best fit the experimental observations. The initial r_2 distance is 2.18Å, the equilibrium C - I distance in ethyl iodide[7], representing a .36Å compression from the C - I distance where the I - CH_2 repulsion drops to zero; the initial r_1 distance is 3.82Å , the resultant of a .50Å extension of the 3.32Å equilibrium Cs - I distance reported in Reference 5.

RESULTS

The solid curves of Figure 2 give the best results of the model. The 19.0 kcal/mole in repulsion is dictated by the necessity of matching the observed CsI CM product speed from the Cs + CH_3I reaction;

this velocity varies, approximately, as the square root of the repulsion over the whole range of I - CH_2 force constants. Figure 2 also presents the results for Cs + I - CH_3 when a more realistic three particle model is used for this reaction; over most of the range in k_2 the two calculations agree, and the slight difference at very high k_2 values is simply due to the greater velocity imparted to the I atom upon recoiling off of the heavier CH_3 group.

For the results presented in Figure 2, it is possible to examine three limiting cases in which the dynamics may be understood as two particle interactions. The first of these, the adiabatic limit, is approached on the far left of the drawing where the I - CH_2 force constant is so weak relative to those of Cs - I and CH_2 - R that these two diatomics separate as if they were single particles. Thus, the full repulsion must appear as kinetic energy of separation, E', so that the CsI CM product speed is given in terms of $\mu_{CsI - CH_2R} = m_{CsI} m_{CH_2R}/M$ $(M = m_{CsI} + m_{CH_2R})$ by

$$u_{CsI} = m_{CsI}^{-1} \left\{ 2P\mu_{CsI - CH_2R} \right\}^{\frac{1}{2}} ; \qquad (2)$$

u_{CsI} can never exceed this limiting value. The striking aspect of Figure 2, with respect to this limit, is the large deviation of the actual calculation from the limit even for the smallest value of k_2 examined. In the second limit, a 3 particle impulsive limit, the I - CH_2 force constant would greatly exceed that of CsI but be less than that of CH_2 - R so that the I atom would recoil from the rigid CH_2R group and thus

$$u_{CsI} = m_{CsI}^{-1} \left\{ 2P\mu_{I - CH_2R} \right\}^{\frac{1}{2}} \tag{3}$$

where $\mu_{I - CH_2R} = m_I m_{CH_2R} / (m_I + m_{CH_2R})$. Although this limit is never reached for the values of k_1 and k_3 chosen here, it indicates the physical origin of the rapid rise shown in Figure 2 of the ethyl, propyl, and butyl iodide curves as k_2 is decreased from its high limit.

The third limit, the two particle impulsive limit, occurs when k_2 becomes much greater than either k_1 or k_3 so that the entire repulsion appears as recoil of I from CH_2; in this case,

$$u_{CsI} = m_{CsI}^{-1} \left\{ 2P\mu_{I-CH_2} \right\}^{\frac{1}{2}} \tag{4}$$

where $\mu_{ICH_2} = m_I m_{CH_2} / (m_I + m_{CH_2})$.

The results of Figure 2 show that this limit is reached for $k_2 \gtrsim 10^6$ dynes/cm where the curves for all four reactions coalesce to the value given by Eg. (4). The qualitative shapes of the curves shown in Figure 2 are similar over a wide range of repulsions from 5 to 25 kcal/mole, although, of course, the magnitude of the CsI speed varies with the repulsion; in particular, the impulsive limit is reached for $k_2 \gtrsim 10^6$ dynes/cm over this entire range of repulsions.

The near equivalence of the experimental CsI CM speeds indicate that the reaction dynamics must be near this impulsive two particle limit.[8] This is of added interest to a model such as that presented here, which no doubt greatly oversimplifies the actual forces, because

at the impulsive limit the energy partitioning is solely dependent on the fraction of the reaction exothermicity released as I - CH_2 impulsive repulsion; thus, the use of such a simple force model to explain small departures from the impulsive limit might be assigned a good deal of credence, whereas application of the same model to another reaction system far removed from this limit might be of much more questionable usefulness. Figure 2 indicates that the slight differences in the experimental CsI CM speeds for these four reactions are best fit by a k_2 somewhat below the impulsive limit, i.e, $k_2 = 2 \times 10^5$ dynes/cm; Table I indicates the qualitative extent of agreement of the experimental data and the model for this value of k_2. Although there is no a priori reason to expect it, it is interesting to note that this value of k_2 is close to the C - I force constant in the alkyl iodides, where $k_{C-I} \approx 2.6 \times 10^5$ dynes/cm.

It is also of interest to examine the partitioning of the product vibrational excitation between Cs - I and CH_2 - R. This data is presented in Figure 3 and the particular values shown in Figure 3 for $k_2 = 2 \times 10^5$ dynes/cm are presented in Table I as well. In the adiabatic limit, CH_2 - R is unexcited and CsI appears with the vibrational energy initially put into Cs - I stretch, $\frac{1}{2}k_1\Delta_1^{(0)^2}$. In the two particle (I - CH_2) impulsive limit, the vibrational excitation in Cs - I and CH_2 - R may once again be calculated from conservation of energy and linear momentum; the curves in Figure 3 are near these limits for $k_2 \gtrsim 10^6$ dynes/cm. Figure 3 illustrates that the Cs - I vibrational excitation is well above the adiabatic limit over the whole range of k_2 values studied. However, the most striking feature of Figure 3

is the very sharp rise in the vibrational excitation of CH_2 - R as k_2 is increased from 1 to 5 x 10^5 dynes/cm. Since this range includes the k_2 value necessary to best fit the CsI CM speed, it suggests that the CH_2-R internal excitation is probably the experimentally measurable energy partitioning parameter which is most sensitive to the form and strength of the I - CH_2 repulsion; unfortunately, this is the energy partitioning parameter which is probably most difficult to determine experimentally.

DISCUSSION

The model presented here is very simplified in many respects: linear, four-particle configuration, no initial translational energy or reactant excitation, and very idealized forces. Ottinger[3] presents arguments to justify a linear model. A more important realization is that these reactions are near the I - CH_2 impulsive limit where the energy partitioning should be independent of the actual intermediate configuration and detailed force laws, and should depend only on the I - CH_2 impulsive energy released. In Ref. 3, the effect of an initial reactant translational kinetic energy was studied and found to be relatively small. The effect of reactant kinetic energy on the present calculations is also readily estimated at the I - CH_2 impulsive limit; an initial relative velocity characteristic of the thermal energy in the experiments causes a decrease in the predicted CsI impulsive limit CM speed from ~ 5% for CH_3I to ~ 17% for C_4H_9I. Thus, incorporation of initial reactant kinetic energy into the calculations would probably allow better agreement with the experiments than is shown in Table I.

Ottinger's[3] calculations for these reactions, based on a similar, but somewhat more sophisticated, one-dimensional linear model, represented the alkyl radical as a chain of CH_2 particles with harmonic binding forces; in addition, a more complex potential function was used to represent the Cs - I - CH_2 interaction. These calculations were unable to match the experimental observations, almost certainly because of the potential energy function employed. For the potential surface of Figure 1, Ottinger's p parameter[3] (ratio of initial I - CH_2 repulsion to Cs - I attraction) has a value of 2.68, which, by his criterion, represents considerably more repulsion than any case examined in Ref. 3. However, in contrast to the results of Ref. 3, the present calculations indicate that the fraction of the exothermicity appearing as product recoil increases monotonically with increasing repulsion P. This characteristic is due to the lack of any "kink in the walls of our potential valley" shown in Figure 1. Thus, the open exit channel of our surface allows the CsI speed to increase monotonically with the progress of the reaction rather than exhibiting the undulations apparent in Figure 5 of Ref. 3. On our surface, the energy in repulsion is released over a short period of time, before the Cs atom or R group has moved appreciably; consequently, the I - CH_2 impulsive limit is approached. In contrast, the trajectories shown in Figure 6 of Ref. 3 indicate that the "kink" in the potential surface employed there prevented a similar behavior and the CsI bond undergoes one half to one full oscillation before reaction is completed.

Another striking difference is the absence of any appreciable alkyl group excitation reported for the calculations of Ref. 3 in contrast to the appreciable alkyl group excitation predicted here. Although the

representation of the alkyl group as a diatomic that is employed here is a rather crude model, the excitation appearing in it should, nevertheless, be indicative of the internal excitation (both rotation and vibration) of the radical in the actual reaction because the reaction is so near the I - CH_2 impulsive limit where conservation laws dictate that the internal excitation in the products can depend only on the impulsive I - CH_2 energy released. Actually, these reactions do deviate somewhat from this impulsive limit and the diatomic representation of the alkyl group employed here should underestimate somewhat the excitation transferred into this radical for a given I - CH_2 energy release; this effect should be more important for the larger radicals.

Raff's [4] three-dimensional trajectory calculations for K + ICH_2CH_3 treated as a four particle reaction system employed a potential energy function chosen to match the early erroneous experimental reports of slow separation of highly excited products.[9] Since most of the energy was released as the reactants approached, Raff observed that the direct interaction trajectories produced large K - I excitation and little energy in either product recoil or internal excitation of the ethyl radical; a similar behavior is observed in the present model as both P and k_2 are decreased. Raff did however also observe a second mode of reaction, via formation of a long-lived complex, in which the ethyl radical was considerably excited; the present calculation failed to reproduce this second reaction mode for any values of P and k_2 considered, undoubtedly due to the lack of any attractive interaction in the r_2 coordinate.

In closing, it is interesting to speculate on the possible implications of the model presented here with reference to the variation in total reactive

cross sections for the M + ICH_3 reactions for differing alkali metals. The Na + ICH_3 reaction is the least exothermic of all of the alkali reactions[6], and indeed ΔD_0 = 19.0 kcal/mole for this reaction. Since this is the amount of energy which must appear in I - CH_2 repulsion, this reaction may be very restricted in the sense that the Na - I distance may be required to decrease all the way to its equilibrium value before reaction can begin; in contrast, the other M + ICH_3 reactions may be initiated at considerably larger M - I distances, consistent with the larger fraction of the exothermicity released as M - I attraction. Thus, within the framework of this model, one might expect a smaller reactive cross section for Na + ICH_3 and indeed, experimentally, the Na + ICH_3 reactive cross section is reported[10] to be considerably smaller than that of Li or K + ICH_3.

REFERENCES

1. This work is reviewed in D. Rapp and T. Kassel, Chem. Rev. 69, 61 (1969).
2. P. J. Kuntz, E. M. Nemeth, and J. C. Polanyi, J. Chem. Phys. 50, 4607 (1969) interpret their exact trajectory calculations of the energy partitioning for these reactions in terms of such a model; D. D. Parrish and R. R. Herm, J. Chem. Phys. 51, 5467 (1969) qualitatively discuss the experimentally observed variations in energy partitioning with changing alkali mass for these reactions in terms of this model.
3. Ch. Ottinger, J. Chem. Phys. 51, 1170 (1969).
4. L. M. Raff, J. Chem. Phys. 44, 1202 (1966); J. Chem. Phys. 50, 2276 (1969).
5. Calculated from ω_e given in J. R. Rusk and W. Gordy, Phys. Rev. 127, 817 (1962).
6. Data taken from: for CsI, L. Brewer and E. Brackett, Chem. Rev. 61, 425 (1961); for CH_3I, G. Herzberg, Molecular Spectra and Molecular Structure (D. Van Nostrand Co., Inc. Princeton, N.J., 1966), Vol. 3.
7. H. J. M. Bowen, ed., Chem. Soc. (London), Spec. Publication 11, M134 (1958).
8. This qualitative explanation was realized in Reference 3 as well.
9. See G. H. Kwei, J. A. Norris, and D. R. Herschbach, J. Chem. Phys. 52, 1317 (1970). This paper traces the evolution of the analysis of the experimental data from relatively low E' value to substantial product translational energy.

10. For Li + ICH_3: D. D. Parrish and R. R. Herm, to be published; for Na + ICH_3: J. H. Birely, E. A. Entemann, R. R. Herm, and K. R. Wilson, J. Chem. Phys. 51, 5461 (1969): for K + ICH_3: Reference 9.

TABLE I

Product Energy Partitioning[a]

Reaction	Experimental[b] CsI CM Velocity	Calculated[c] CsI CM Velocity	CsI Vibration Energy	CH_2-R Vibration Energy
Cs + ICH_3	1.73	1.74	11.49	.03
Cs + IC_2H_5	2.05	1.96	12.03	4.77
Cs + IC_3H_7	2.09	2.10	12.41	6.71
Cs + IC_4H_9	2.00	2.32	13.15	6.32

(a) Vibrational energies are given in kcal/mole, CsI CM velocities in units of 10^4 cm/sec.

(b) Experimental results cited in Ref. 3.

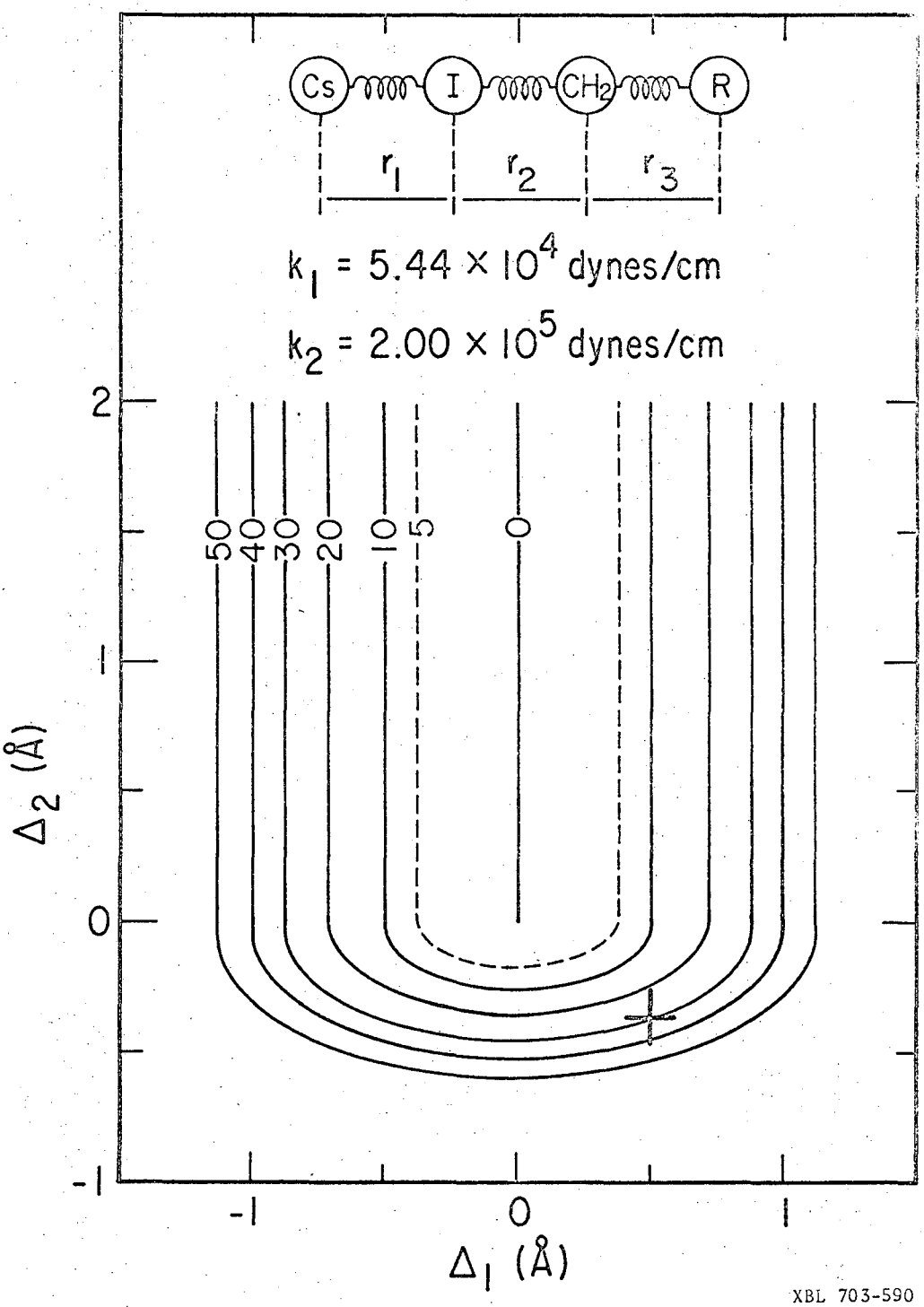
(c) Results for exothermicity = 28.7 kcal/mole, repulsion = 19.0 kcal/mole, and I - CH_2 force constant = 2.0×10^5 dynes/cm.

FIGURE CAPTIONS

Fig. 1. Effective potential energy surface, with energies given in kcal/mole, for r_3 held at its equilibrium configuration. The " + " mark denotes the starting point of a reactive trajectory for 19.0 kcal/mole repulsion; Δ_i equals the displacement of r_i from its equilibrium value.

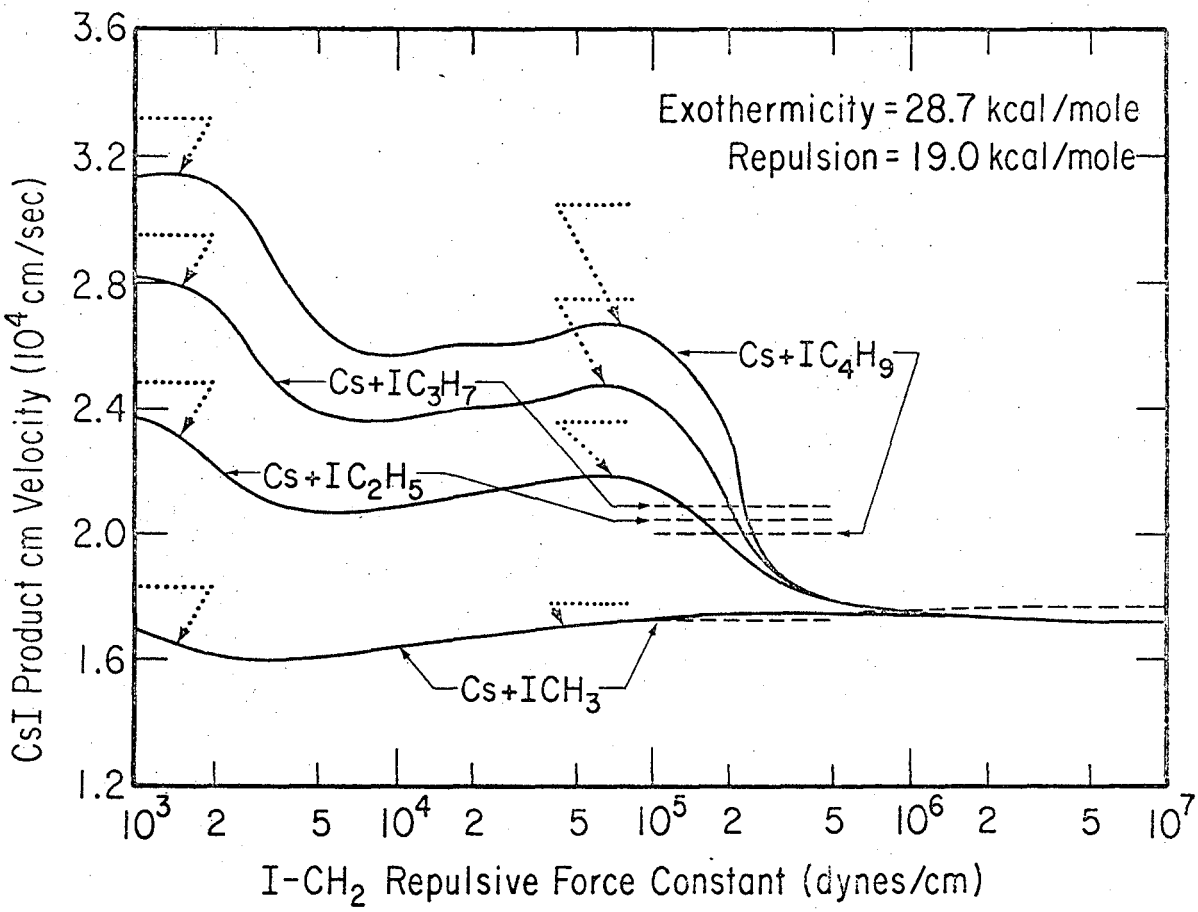
Fig. 2. Plot of product CsI CM speed versus the I - CH_2 force constant for 19.0 kcal/mole repulsion. The solid curves give the results of the four particle Cs - I - CH_2 - R calculations. The dashed curve deviating from the Cs - I - CH_2 - H solid curve for high force constant values presents the results of a three particle calculation for Cs - I - CH_3; at lower force constants, this is indistinguihable from the four particle calculation. The dashed lines give the experimentally observed CsI CM speeds cited in Ref. 3. The dotted lines on the left give the adiabatic limits, where the repulsion is released so slowly that it must all appear as product translational energy. The dotted lines in the middle of the force constant range give the three particle impulsive limit (never reached) in which the I impulsively kicks off of the "CH_2 - R particle."

Fig. 3. Vibrational excitation of the product diatomics: solid curves for Cs - I and long-dashed curves for CH_2 - R. The short-dashed lines at the limiting low and high I - CH_2 force constants give the adiabatic and two particle impulsive limits for the Cs - I excitation.



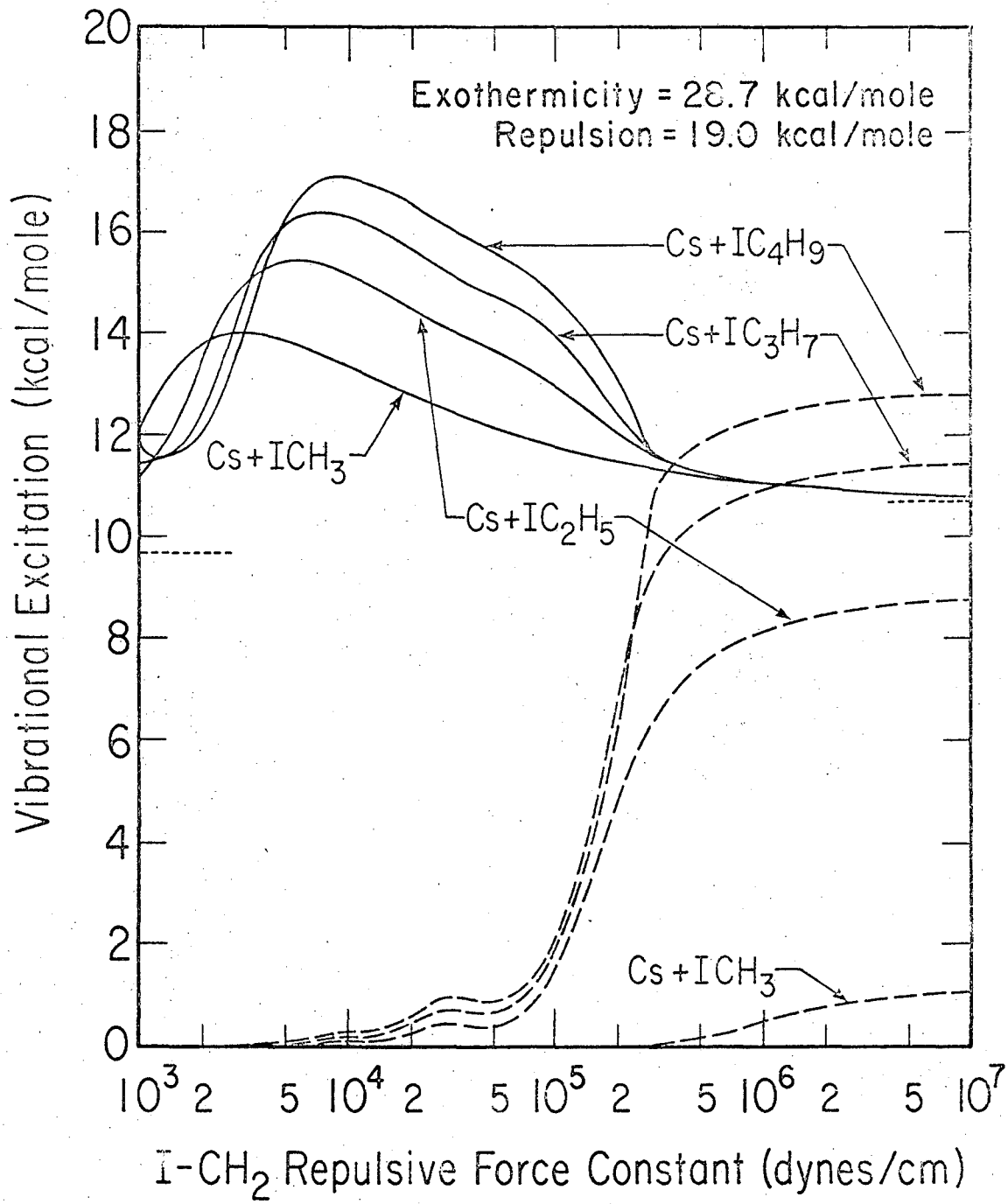
XBL 703-590

Fig. 1



XBL 703-492

Fig. 2



XBL 703 -491

Fig. 3

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720