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PL-TR-92-2132

# MODELING OF ATOM-DIATOM SCATTERING

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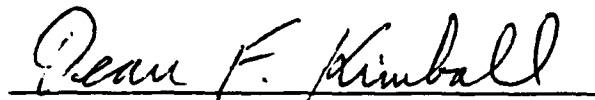
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30 May 1992

Scientific Report No. 3

**PHILLIPS LABORATORY**
Directorate of Geophysics
**AIR FORCE SYSTEMS COMMAND**
**HANSCOM AIR FORCE BASE, MA 01731-5000**

93-02348

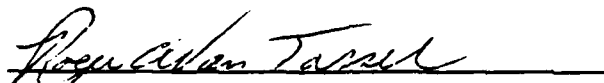$\| \| \| \| \| \| \| \| \| \| \| \| \|$

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# REPORT DOCUMENTATION PAGE

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| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE 30 May 1992 | 3. REPORT TYPE AND DATES COVERED Scientific Report No. 3 |
|---|---|---|

| 4. TITLE AND SUBTITLE Modeling of Atom-Diatom Scattering | 5. FUNDING NUMBERS PE 63220C PR S322 TA 03 WU AM Contract F19628-89-C-0033 |
|---|---|
| 6. AUTHOR(S) J.M. Sindoni | |

| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Yap Analytics, Inc. 594 Marrett Road Lexington, MA 02173 | 8. PERFORMING ORGANIZATION REPORT NUMBER YAI-TR-106 |
|---|---|

| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Phillips Laboratory Hanscom AFB, MA 01731-5000 Contract Manager : Dean Kimball/GPOS | 10. SPONSORING/MONITORING AGENCY REPORT NUMBER PL-TR-92-2132 |
|---|---|

**11. SUPPLEMENTARY NOTES**

| 12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited | 12b. DISTRIBUTION CODE |
|---|---|

**13. ABSTRACT** (Maximum 200 words)

This report entails the work performed on modeling atom-diatom scattering processes utilizing the Impulse Approach (IA). Results of the model, obtained with a computer code, have proven to be in remarkable agreement with laboratory measurements for several atom-diatom scattering systems. Two scattering systems, in particular, that were successfully modeled and compared to measurements were Ar-KBr and Ar-CsF. The IA model provided an explanation for the rapid deactivation evident in the Ar-KBr system. Experimental results in the Ar-CsF experiment that could not be explained by conventional models were also sucessfully modeled using the IA. Results fit the experimental observations.

| 14. SUBJECT TERMS Impulse Approach | Upper Atmosphere IR Radiation Ballistic Collision | 15. NUMBER OF PAGES 46 |
|---|---|---|
| | | 16. PRICE CODE |

| 17. SECURITY CLASSIFICATION OF REPORT Unclassified | 18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified | 19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified | 20. LIMITATION OF ABSTRACT SAR |
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NSN 7540-01-280-5500

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# MODELING OF ATOM-DIATOM SCATTERING

## 1.0 INTRODUCTION:

During the past year, Yap Analytics, Inc. has advanced the understanding of atom-diatom scattering processes. Utilizing the theory known as the Impulse Approximation (IA), we have produced remarkable agreement with laboratory measurements for several atom-diatom scattering systems. Two scattering systems which we have modeled quite successfully are Ar-KBr and Ar-CsF. Both systems have been studied experimentally by cross beam techniques. The experiment involving the Ar-KBr system consisted of a beam of highly-vibrationally excited KBr crossed with a slow moving beam of Ar with a relative translational energy (RTE) of about 0.04 eV.[1-4] A great degree of vibrational relaxation of KBr was evident in this system and could not be explained by existing theories. Applying the IA to this system has provided an explanation of this rapid deactivation.[5] In the Ar-CsF experiment, a beam of Ar atoms was crossed with a beam of CsF molecules at a relative translational energy of about 1 eV.[6-8] A feature of the measured results that could not be explained was that almost all of the available 1 eV RTE may be converted into vibrational/rotational energy of CsF. This system has also been successfully modeled using the IA.[9] It is important to note that the processes involved in these two systems are very different. In the Ar-KBr system, the energy transferred during the collision is primarily from vibrational motion of the diatom to relative translational energy. In the Ar-CsF system, the energy is converted from relative translational to vibrational/rotational energy. That the IA can be used to describe these two very distinct scattering systems strengthens the assertion that the IA may be successfully applied to a broad range of atom-diatom scattering processes.

In addition to providing agreement with laboratory measurements for the Ar-KBr and Ar-CsF scattering systems, we have made a further contribution to the study of crossed beam chemical re-

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actions and energy transfer processes by presenting a method for producing state-selected molecular beams.[10] The method is based on the ballistic phenomenon found in the Ar-CsF system.

Although the IA has been proven successful in describing a number of scattering systems, we have recognized some of the shortcomings of our existing impulse theory, such as the need to include multiple-collision terms for certain scattering systems and the limitations of using a hard core atom-atom potential. We have subsequently taken steps toward developing the IA into a more rigorous model.

Progress and results of our work were published in the open literature and are also included in appendices (A-C). A summary of each of the publications is included in the following sections.

## 2.0 RELAXATION OF HIGHLY VIBRATIONALLY EXCITED KBR BY AR

Using the IA, we have successfully described the deexcitation of highly vibrationally excited KBr, upon colliding with Ar, at a relative translational energy of about 0.05 eV.[5] In the experiments involving this scattering system it was found that a substantial fraction of the roughly 2 eV KBr internal energy may be converted into translational energy of motion in a single collision.[1-4] Existing theories were not able to account for this degree of vibrational deexcitation. Three-dimensional classical trajectory calculations using various potential-energy surfaces underestimate highly inelastic scattering of KBr by Ar.[11] We have shown that the IA, using hard core Ar-K+ and Ar-Br- two-body potentials, successfully predicts the relaxation of KBr in these experiments. One characteristic of the scattering that is not reproduced in such a calculation is a dip in the cross-section, especially pronounced for the center of mass (c.m.) scattering angle of 60 degree, that occurs at a c.m. recoil velocity of about 400 m/s. We have suggested that this discrepancy may be the result of the hard core two-body poten-

tial. It is believed that a more realistic potential may yield a more complete agreement with the experiment, especially considering the smallness of the relative translational energy.

## 3.0 MECHANISM OF BALLISTIC COLLISIONS

Additionally, we have had remarkable success predicting the scattering of CsF upon colliding with Ar, at a relative translational energy of about 1 eV.[9] Crossed beam experiments involving these collision partners show that almost all of the roughly 1 eV relative translational energy may be converted into rotational and vibrational energy of CsF.[6-8] Until now, the process responsible for this phenomenon, called the ballistic effect, was not well understood. Using our previously developed IA programs, we computed differential cross sections for the three systems studied experimentally: Ar-CsF, Ar-$I_2$, and Ar-CsI. The differential cross sections were computed with respect to the c.m. of the coliding particles. To compare our calculations to the laboratory measurements required that we transform our results to the laboratory coordinate system. This turned out to be a vital step toward understanding the experimental results. We derived equations for this transformation, known as the Jacobian of transformation, that are quite different from those given in literature.[12] Because the Jacobian of transformation is a fundamental relationship which is prevalent in scattering theory, we view this finding in itself as a significant contribution to the understanding of crossed beam scattering processes. The IA proved successful in predicting the ballistic effect for the Ar-CsF system and the non-existence of the ballistic effect in the Ar-$I_2$ system. However, it was not able to reproduce the ballistic effect for the Ar-CsI system. We have begun to modify the IA formalism to include double-collision terms. We believe this will enable the theory to predict the ballistic effect for the Ar-CsI system.

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## 4.0 A PROPOSAL TO PRODUCE VELOCITY-SELECTED AND STATE-SELECTED MOLECULAR BEAMS USING THE BALLISTIC EFFECT

We have recently proposed a method to produce velocity-selected and state-selected molecular beams using the ballistic effect.[10] The ballistic peak in the Ar-CsF system was shown to consist of only several vibrational/rotational transitions, whereas several hundred transitions comprise the pseudoelastic peak.[9] The ballistic transitions have a much larger differential cross section in the laboratory frame because of a greater Jacobian of transformation from the c.m. to the laboratory coordinates. It is the Jacobian of transformation, and not a property specific to CsF, that produces the ballistic effect. Thus, one should expect that the ballistic effect should be observable for every atom-molecule system under suitable conditions. According to our theory, when the relative translational energy equals the energy of one of the rotation-vibration transitions, this transition may have a differential cross section as much as an order of magnitude greater than that of any other neighboring transitions. The parent beam velocities can be chosen to produce any desired relative translational energy, thereby allowing the production of a state-selected beam traveling at the velocity of the c.m. The ability to produce state-selected beams would greatly improve the understanding of crossed beam chemical reactions and energy transfer processes.

## 5.0 FUTURE WORK

Although the IA has been shown to describe certain atom-diatom scattering processes quite well, there are many scattering processes which the IA cannot adequately model. For instance, while the IA has explained the high degree of vibrational deexcitation of KBr by Ar, the computed cross sections for this system do not reproduce the dip in the cross section that occurs at a c.m. recoil velocity of about 400 m/s. We are investigating the possibility that this dip in the cross sec-

tions is due to a long-range attractive potential between Ar and each of the atoms that comprise KBr. Such a potential plays an important role for near-elastic scattering at small c.m. scattering angles. We intend to develop computer programs which use atom-atom potentials more sophisticated than the pr ;ently utilized hard core repulsive potentials.

One of the basic assumptions of the impulse theory is that during the collision process the incident atom collides only with one end of the diatom. The operator which describes the energy transfer process that occurs during the collision of the incident atom with the diatom is known as the three-body T matrix. The impulse theory reduces the three-body T matrix to include only those terms representing collisions with only one end of the diatom. The result, called the two-body T matrix, has been used in all of our calculations to date. The two-body T matrix ignores the possibility of collisions in which the incident atom collides with one end of the diatom, and then collides with the other end. We believe that this reduction may be responsible for the theory's inability to predict a ballistic effect for the Ar-CsI system, as well as its inability to reproduce the correct final rotational distributions of $N_2$ after colliding with $Li^+$ at a relative translational energy of 4-7 eV. The two ends of CsF and of $N_2$ are similar in mass, making the possibility of multiple collisions seem greater. We have several approaches to developing the theory to include the multiple collision terms. One approach is to compute the single and double collision terms and disregard triple and higher collision terms. The second approach involves replacing the diatom by a potential located at its center and replacing the incoming particle with a distorted wave. Both methods, now under development, are computationally challenging, but offer viable alternatives to the single-collision formalism. This represents the first attempt at a fully-quantum impulse calculation in which multiple collision terms are considered.

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**REFERENCES**

1.  M.S. Chou, F.F. Crim and G.A. Fisk, "Inelastic Scattering of Vibrationally Excited KBr by Ar and $CO_2$," <u>Chem. Phys. Lett.</u> 20, 464 (1973).

2.  F.F. Crim, M.S. Chou and G.A. Fisk, "Inelastic Scattering of Vibrationally Excited KBr by Small Nonpolar and Essentially Nonpolar Partners," <u>Chem. Phys.</u> 2, 283 (1973).

3.  T. Donahue, M.S. Chou and G.A. Fisk, "Inelastic Scattering of Vibrationally Excited KBr by Small Polar Molecules," <u>Chem. Phys.</u> 2, 271 (1973).

4.  T. Donahue, M.S. Chou and G.A. Fisk, "Inelastic Scattering of Vibrationally Excited KBr by $CH_3OH$," <u>J. Chem. Phys.</u> 57, 2210 (1972) .

5.  R.D. Sharma and J.M. Sindoni, "Relaxation of Highly Vibrationally Excited KBr by Ar," <u>Phys Rev.A</u>, 45, 521 (1992).

6.  H.J. Loesch and D.R. Herschbach, "Ballistic Mechanism for Vibrational and Rotational Energy Transfer in Ar + CsI Collisions,"<u>J. Chem. Phys.</u> 57,2038 (1972).

7.  D.L. King, H.J. Loesch and D.R. Herschbach, <u>Dis. Faraday Soc.</u> 55, II-34 (1973).

8.  D.L. King, "Facile Four-Center and Six-Center Reactions," Ph.D. Thesis, Chemistry Depart., Harvard University (1974).

9.  J.M. Sindoni and R.D. Sharma, "Mechanism of Ballistic Collisions," <u>Phys. Rev. A</u> 45, R2659 (1992).

10. J.M. Sindoni and R.D. Sharma, "A Proposal to Produce Velocity-Selected and State-Selected Molecular Beams Using the Ballistic Effect,"J.Chem. Phys. (to be published).

11. M. Keith Matzen and G.A. Fisk, "A Classical Trajectory Study of Inelastic Collisions Between Highly Vibrationally Excited KBr and Ar,"J. Chem. Phys. 66, 1514 (1977).

12. R.D. Sharma and J.M. Sindoni, "Inelastic and Ballistic Processes Resulting from CsF-Ar Collisions," J. Chem. Phys. (to be published)

APPENDIX A

# RELAXATION OF HIGHLY VIBRATIONALLY EXCITED KBr BY Ar. [*]

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and

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Exact formulation of the impulse approach (IA), also known as the quantum mechanical spectator model, is used to investigate the rapid deactivation of highly internally excited KBr, written as KBr[**], by Ar - a phenomenon not previously understood. The model of inelastic scattering at the repulsive wall, approximated here by a hard core potential, using the impulse formalism is compared with the experimentally observed results obtained by scattering KBr[**] with Ar. The calculation is in excellent agreement with the measured results for the 75° center-of-mass (CM) scattering angle, while the calculated results for the 45° CM scattering near the peak (nearly elastic scattering) are a factor of about 1.5 smaller than the measured results. This, we believe, is the first impulse calculation where the collision energy is supplied by the internal motion of the target and not by the translational motion of the projectile.

PACS numbers: 03.80.+r, 34.50.-s

The last thirty years have seen a great deal of progress in the understanding of elementary collision processes[1]. The underlying mechanism for the relaxation of highly vibrationally and rotationally excited molecules, however, remains elusive. Fisk and students[2-5] in a series of papers have reported the relaxation of highly vibrationally excited KBr, denoted by KBr**, by various collision partners. KBr** produced by the reaction of K with $Br_2$ in a crossed molecular beam[6] has about 41 kcal/mole of vibrational energy (average vibrational quantum number $\approx 90$ ) and is described by a rotational temperature of roughly 1500 °K (average rotational quantum number $\approx$ 126). The KBr** beam thus produced is again crossed with another beam which may consist of Ar, $N_2$, CO or other molecules at a modest collision energy of about 1 kcal/mole (roughly 0.04 eV). The relative differential cross section for the deactivation of KBr** as a function of KBr recoil velocity for several scattering angles is measured for various collision partners. There are small differences in the shape of the curves for the relative differential cross section for different collision partners, but the important result of the experiments is that a substantial fraction of the roughly 2 eV internal energy may be converted into translational energy of relative motion in a single collision. This is not to imply that none of the internal energy of KBr** ends up as vibrational/rotational energy of its molecular collision partner. In fact, smaller recoil velocities of KBr during collision of KBr** with $CO_2$ than with Ar may be the result of additional channels available resulting from the collision with $CO_2$. The conclusion is that the vibrational and rotational quantum numbers of KBr** change by several tens during a single collision. Further, the large changes in the internal quantum numbers occur with appreciable probability. For example, during a collision with Ar at a CM scattering angle of 75°, the probability of KBr acquiring a CM recoil velocity of 1 km/s is about 1/4 as large as the probability of having a near elastic CM recoil velocity of 0.2 km/s. The corresponding ratio at a CM scattering angle of 45° is about 1/10. It

is not possible to reconcile these observations with the existing theories[1] . Three-dimensional classical trajectory calculations using various potential energy surfaces underestimate highly inelastic scattering of $KBr^{**}$ by $Ar^{7}$.

Relaxation of the vibrational degree of freedom, simply called V-T process, is described by the Landau-Teller[1,8] model. This model for atom-diatom collisions approximates atom-diatom interaction potential by the sum of the atom-atom potentials. In addition, it assumes that the time duration of the collision is much smaller than the period of internal motion. Both these assumptions are well known to the students of scattering theory as the impulse approximation (IA). L-T is a one dimensional model in which rotations play no role. This model, of course, can not be used to calculate differential cross sections. In this letter we show how an exact IA calculation developed earlier[9] can be used to theoretically calculate the differential cross sections measured by Fisk and students[2-5].

The impulse approach, as formulated by Chew et al.[10-12], has been applied to the vibrational-rotational excitation of a diatom during its collision with energetic atoms by Bogan[13], Eckelt et al.[14-17] and by Beard and Micha[18]. The basic premises of IA have already been mentioned. It has been shown by the present authors that the resulting equations can be solved exactly[9] without resorting to the peaking approximation. One benefit of the exact solution, in contrast to the peaking approximation where the two-body t-matrix is evaluated for a given value of the spectator momentum and which had been used in all of the earlier atom-diatom studies[13-18], is that the relative momentum, $\vec{p}_3$, and the intramolecular momentum due to vibrational-rotational motion, $\vec{q}_3$, enter the formulation on an equal footing. This permits a solution of the problem where the collision energy is provided by the vibrational-rotational motion of the diatom rather than the relative translational energy of the atom-diatom motion. The expression for the differential cross section is given elsewhere[9] and will not be repeated here. We use a hard core potential to represent the atom-atom interaction. For the internal energies

under consideration the lowest state is ionic[19]. We approximate the Ar-K$^+$ and Ar-Br$^-$ hard core radii by the corresponding values for Ar-Ar and Ar-Kr, respectively. The latter parameters were taken from Hirschfelder, Curtiss and Bird[20]. The sensitivity of the calculation to this approximate potential is discussed later. Having selected the potential we carry out an exact impulse calculation[9]. The KBr$^{**}$ wave functions were obtained using a potential function constructed from spectroscopic constants[21] and extrapolation by a Padé [2,2] approximant[22], adding the centrifugal term to obtain the effective potential energy curve.

Figure 1 is a plot of the differential scattering cross section (cm$^2$/sterad), at a CM scattering angle of 75°, for vibrationally elastic scattering of KBr(v=90,j=126) by Ar, as a function of j' (filled circles). Also shown are the contributions to the cross section by collision of Ar with Br$^-$ (squares) and K$^+$ (triangles). In addition to the peak due to elastic scattering, the Ar-Br$^-$ cross section shows supernumerary rotational rainbows and a rotational rainbow[23] at j'=70. Cross section for scattering of K$^+$ alone by Ar gradually decreases from the peak at elastic scattering. The scattering amplitudes from the two scattering centers interfere constructively for even $\Delta j$ and destructively for odd $\Delta j$. This interference as well as the rotational rainbows give rise to the complicated pattern for the variation of the differential cross section (filled circles) for the Ar-KBr system. It should be noted that the scattering from K$^+$ dominates for large $\Delta j$ while the scattering from Br$^-$ makes a larger contribution for smaller $\Delta j$. This is entirely appropriate since K$^+$ is farther from the CM of the molecule than Br$^-$ and a given change in the relative momentum leads to greater torque during a collision of Ar with K$^+$. Near the elastic peak the scattering from Br$^-$ dominates because of the large Br$^-$-Ar hard core collision diameter. The cross section drops sharply when j' exceeds 140 because the available translational energy is almost used up. The differential cross section at the CM scattering angle of 45° shows modulations similar to those observed 75°. The only difference is that the rotational rainbows appear at smaller values of $\Delta j$.

Again, this is reasonable because a given change in the linear momentum produces a larger torque at 75° than at 45°.

Figure 2 gives the same plot as in figure 1 for the final vibrational level 50. The theory of rainbows for the vibrational-rotational transitions is under development[24]. The structure of the differential cross section as a function of j' is understandably more complicated than that found in the very instructive earlier study[23] of rotational rainbows in the vibrationally elastic situation. The Ar-$K^+$ differential cross section clearly shows several supernumerary rainbows and a rainbow at j'=240. The reason for large variations in the differential cross section in the j'=80 to j'=130 region for the Ar-$Br^-$ system and almost no variations at all for the Ar-$K^+$ system is not yet completely understood. It appears related to the fact that for a given change in the rotational quantum number a larger change in the quantum number for the orbital motion, and a greater change in the phase, is required for the Ar-$Br^-$ collision than for the Ar-$K^+$ collision. The scattering from $K^+$ again makes the dominant contribution to the cross section for large changes in $\Delta j$. Also, even for small changes in the rotational quantum number it is not much smaller than for scattering from $Br^-$. It is also seen that, compared to the vibrationally elastic scattering, the differential cross section is only smaller by less than a factor of about 10 for v'=50 when about 40% of the vibrational energy is converted into translational energy of relative motion. Our model reproduces the experimental observation that large vibrational quantum number changes take place with significant probability. For the CM scattering angle of 45°, the scattering from $Br^-$ may be neglected.

Figure 3 is a plot of measured and calculated differential cross sections as a function of KBr recoil velocity in the CM system for a CM scattering angle of 75°, the largest scattering angle for which measurements are available. The calculated differential cross sections in this figure as well as in the previous ones took $K^+$-Ar and $Br^-$-Ar hard core radii to be 3.40 and 3.85 Å, respectively. The maximum of the measured relative

differential cross section is normalized to agree with the peak of the calculated cross section. The calculated differential cross sections were averaged over an interval of 50 m/s of the KBr CM recoil velocity. The agreement between the calculation and the experiment is remarkable. Also shown in figure 3 are the results due to scattering by $K^+$ alone and $Br^-$ alone. For nearly elastic collisions scattering due to $Br^-$ makes a larger contribution while for highly inelastic collisions (the ones with large KBr recoil velocity), only the contribution from $K^+$ is important. When the $K^+$-Ar and $Br^-$-Ar hard core radii are taken to be 4.81 and 5.44 Å, respectively, only the magnitude of the calculated differential cross section changes; the shape of the curve for the differential cross section curve as a function of the KBr recoil velocity remains unchanged. Similar results were obtained when the two hard core radii were taken to be 3.40 and 5.44 Å.

Figure 4 gives a plot of the differential cross section as a function of the KBr recoil velocity for the CM scattering angle of 45°, the smallest angle for which the experimental observations are available. The curves plotted are for scattering of Ar by KBr, $K^+$, $Br^-$ as well as the experimentally observed results. Now the comparison between the calculations and measured results is absolute, the normalization factor being determined in figure 3. Highly inelastic collisions are again well described as due to scattering of Ar by $K^+$ alone. Nearly elastic scattering is underestimated by the calculation. This appears to be due to using a very simple model potential and ignoring the attractive part of the atom-ion potentials. This may also be the reason that the dip in the differential cross section at about 350 m/s KBr recoil velocity is not reproduced by the calculation.

In summary, our model of the relaxation of highly internally excited $KBr^{**}$ during collision with Ar yields good agreement with the measured values at a CM scattering angle of 75°. The comparison with the experimental measurements for 45° CM scattering angle yields good agreement for large KBr recoil velocity, while the calculation underestimates the nearly elastic experimental results by a factor of about

1.5. This is probably due to the neglect of the long range attractive potential, which plays an important role for near elastic scattering at small CM scattering angles. Finally, because there are so many closely spaced final states involved in the calculation, the KBr recoil velocity distribution as a function of the calculated differential cross section is dependent only on the relative magnitudes and not on the shape of the state-to-state differential cross sections. This, we believe, makes the shape of the calculated KBr recoil velocity distribution rather insensitive to the hard core parameters used.

Thus the first application of the IA to a situation where the collision energy is provided by the internal motion of the target also marks the first explanation of the observed rapid deactivation of highly excited KBr**.

REFERENCES

1. R. D. Levine and R. B. Bernstein, "Molecular Reaction Dynamics," Oxford University Press, New York, Second Edition (1987).

2. M.S. Chou, F.F. Crim and G.A. Fisk, "Inelastic Scattering of Vibrationally Excited KBr by Ar and $CO_2$," Chem. Phys. Lett., 20: 464 (1973).

3. F.F. Crim, M.S. Chou and G.A. Fisk, "Inelastic Scattering of Vibrationally Excited KBr by Small Nonpolar and Essentially Nonpolar Partners," Chem. Phys., 2: 283, (1973).

4. T. Donahue, M.S Chou and G.A. Fisk "Inelastic Scattering of Vibrationally Excited KBr by Small Polar Molecules," Chem. Phys., 2: 271, (1973).

5. T. Donahue, M.S. Chou and G.A. Fisk, "Inelastic Scattering of Vibrationally Excited KBr by $CH_3OH$," Chem. Phys., 57: 2210, (1972).

6. C. Matzen and D.R. Herschenbach, Discussions of Faraday Society, 44: 176 (1967);
J.H. Birely and D.R. Herschenbach, "Reactive Scattering in Molecular Beams: Velocity Analysis of KBr Formed in the $K+Br_2$ Reaction," J. Chem. Phys., 44: 1690 (1966).

7. M. Keith Matzen and G.A. Fisk, "A Classical Trajectory Study of Inelastic Collisions Between Highly Vibrationally Excited KBr and Ar," J. Chem. Phys., 66: 1514, (1977).

8. L.D. Landau and E. Teller, Physik Z. Sowjetunion, 100: 34 (1936).

9. R.D. Sharma, P.M. Bakshih and J.M,. Sindoni, "Impulse Formalism for Atom-Diatom Collisions," Phys. Rev. A, 43: 189 (1991). See also M.S. Gravielle and J.E. Miraglia, "Electron Capture in Assymetric Collisions," Phys. Rev. A, 38: 5034 (1988).

10. G.F. Chew, "The Inelastic Scattering of High Energy Neutrons by Deuterons According to the Impulse Approximation," Phys. Rev., 80: 196 (1950).

11. G.F. Chew and G.C. Wick, "The Impulse Approximation," Phys. Rev., 85: 636 (1952).

12. G.F.Chew and M.L. Goldberger, "The Scattering of Elementary Particles by Complex Nuclei - a Generalization of the Impulse Approximation," Phys. Rev., 87: 778 (1952). See also

J. Ashkin and G.C. Wick, "Comment on the "Impulse Approxima-tion," Phys. Rev., 85: 686 (1952).

13. A. Bogann, Jr. "Impulse Approximation for Three-Dimensional Inelastic Atom-Diatom-Molecule Collisions," Phys. Rev. A 9: 1230 (1974).

14. P. Eckelt, H.J. Korsch and V. Phillipp, "Energy Loss Spec-tra for Vibro-Rotational Molecular Excitation in an Impul-sive Spectator Model," J. Phys. B: Atom Molec. Phys., 7: 1649 (1974).

15. H.J. Korsch and V. Phillipp, "Quantum-Mechanical Impulse Approximation for Vibro-Rotational Excitation in Atom-Dia-tom Collisions," Phys. Rev.A, 13: 497 (1976).

16. V. Phillipp, H.J. Korsch and P. Eckelt, "Inelastic Atom-Diatom-Molecule Collisions I: Influence of Mass Asymmetry of Heteronuclear Molecules," J. Phys. B: Atom. Molec. Phys., 9: 345 (1976).

17. V. Phillipp, H.J. Korsch and P. Eckelt, "Inelastic Atom-Diatomic-Molecule Collisions II: Influence of Initial Vi-brational and Rotational Excitation," J. Phys. B: Atom. Molec. Phys., 10: 117 (1977).

18. L.H. Beard and D.A. Micha, "Collision Dynamics of Three In-teracting Hyperthermal Collisions,"J. Chem. Phys., 74: 6700 (1981).

19. Alkali Hallide Vapors Structure, Spectra and Reaction Dyna-mics, eds. P. Davidovits and D.L. McFadden, Academic Press, New York (1970), Chapt. 3, "Optical Spectra of the Alkali Halide Molecules by R. Stephen Berry.

20. J. O. Hirschfelder, C.F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids John Wiley and Sons, Inc., New York (1954).

21. K. P. Hubeer and G. Herzberg Constants of Diatomic Mole-cules, Van Nostrand Reinhold Company, New York (1979).

22. Alkali Halide Vapors Structure, Spectra and Reaction Dyna-mics, eds. P. Davidovits and D. L. McFadden, Academic Press, New York (1979), Chapt. 15 "Structure of Alkali Halides: Theoretical Methods" by Kenneth D. Jordan.

23. Molecular Collision Dynamics, ed. J. M. Bowman, Springer-Verlag, New York (1983), Chapt. 4 "Rotational Rainbows in Atom-Diatom Scattering" by R. Schinke and J. M. Bowman.

24. R. Sharma and J. Sindoni, In Preparation.

## FIGURE CAPTIONS

Figure 1. Calculated differential cross section for scattering of KBr ($v=90, j=126$) by Ar with relative translational energy of 1 kcal/mole at a center-of-mass (CM) scattering angle of 75° and final vibrational quantum number $v'=90$ as a function of the final rotational quantum number ($j'$).

Figure 2. Calculated differential cross section for scattering of KBr ($v=90, j=126$) by Ar with relative translational energy of 1 kcal/mole at a CM scattering angle of 75° as a function of the final rotational quantum number ($j'$) for $v'=50$ ($\Delta v = -40$).

Figure 3. Calculated and measured differential cross section for scattering of KBr ($v=90, j=126$) by Ar with relative translational energy of 1 kcal/mole at a CM scattering angle of 75° as a function of the CM recoil velocity of KBr. The peak of the measured cross section is normalized to agree with the peak of the calculated cross section. The hard core radii used are 3.40 Å for $K^+$-Ar and 3.85 Å for $Br^-$-Ar. The four curves plotted are : 1. Experimental measurements (dotted line). 2. Ar-KBr calculation (solid line). 3. Ar-$K^+$ calculation (spaced dashed line). 4. Ar-Br- (dash-dot line).

Figure 4. Same as in figure 3 except the CM scattering angle is 45°. The cross sections plotted are now absolute. The normalization is taken from figure 3.
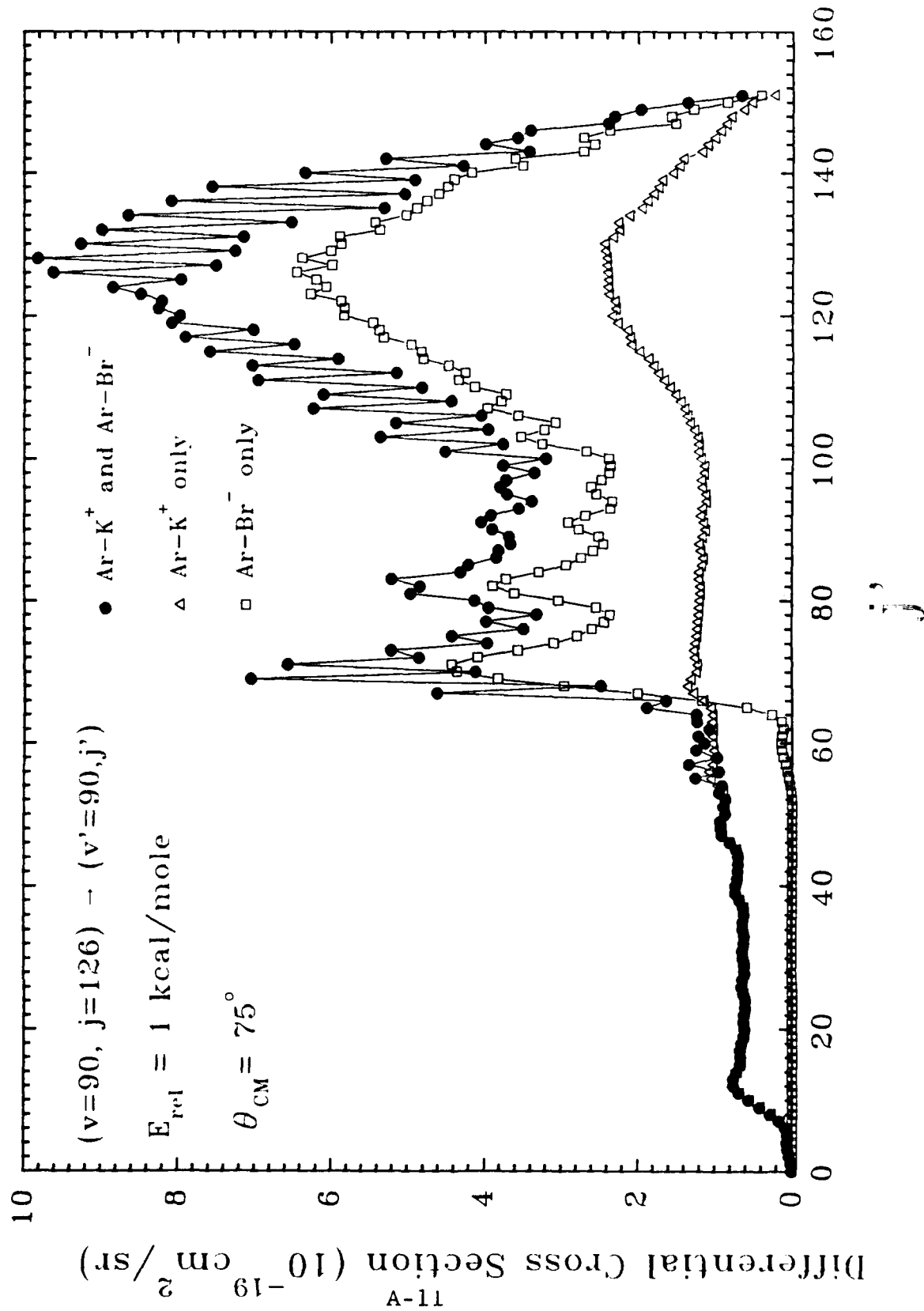
Figure 1

$(v=90, j=126) \to (v'=90, j')$

$E_{rel} = 1$ kcal/mole

$\theta_{CM} = 75°$

Differential Cross Section ($10^{-19}$ cm$^2$/sr)

j'

● Ar–K$^+$ and Ar–Br$^-$

△ Ar–K$^+$ only

□ Ar–Br$^-$ only

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Figure 2

$(v=90, j=126) \rightarrow (v'=50, j')$

$E_{rel} = 1 \text{ kcal/mole}$

$\theta_{CM} = 75^\circ$

• $Ar\text{-}K^+$ and $Ar\text{-}Br^-$

△ $Ar\text{-}K^+$ only

□ $Ar\text{-}Br^-$ only

Differential Cross Section ($10^{-20} \text{cm}^2$/sr)

j'

A-12

Figure 3

$(v=90, \, j=126) \rightarrow (v',j')$

$E_{rel} = 1$ kcal/mole

$\theta_{CM} = 75°$

—— Ar–K$^+$ and Ar–Br$^-$
-------- Ar–K$^+$ only
—·—· Ar–Br$^-$ only
········ Experimental (normalized)

KBr C.M. Recoil Velocity (m/s)

Differential Cross Section ($10^{-16}$ cm$^2$/sr)

A-13

$(v=90, j=126) \rightarrow (v',j')$

$E_{rel} = 1 \text{ kcal/mole}$

$\theta_{CM} = 45°$

—— Ar–K$^+$ and Ar–Br$^-$

----- Ar–K$^+$ only

—·—· Ar–Br$^-$ only

········· Experimental

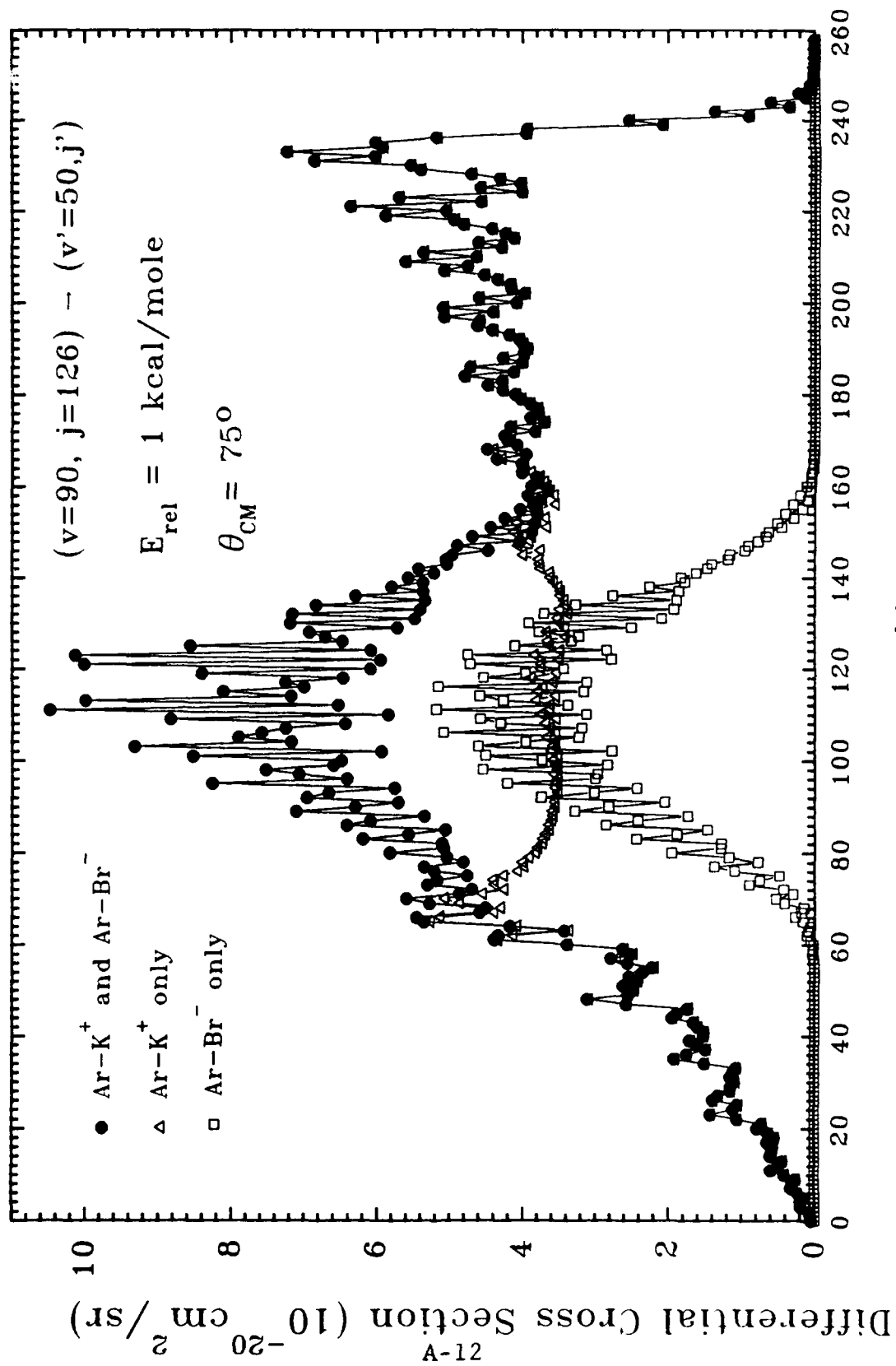KBr C.M. Recoil Velocity (m/s)
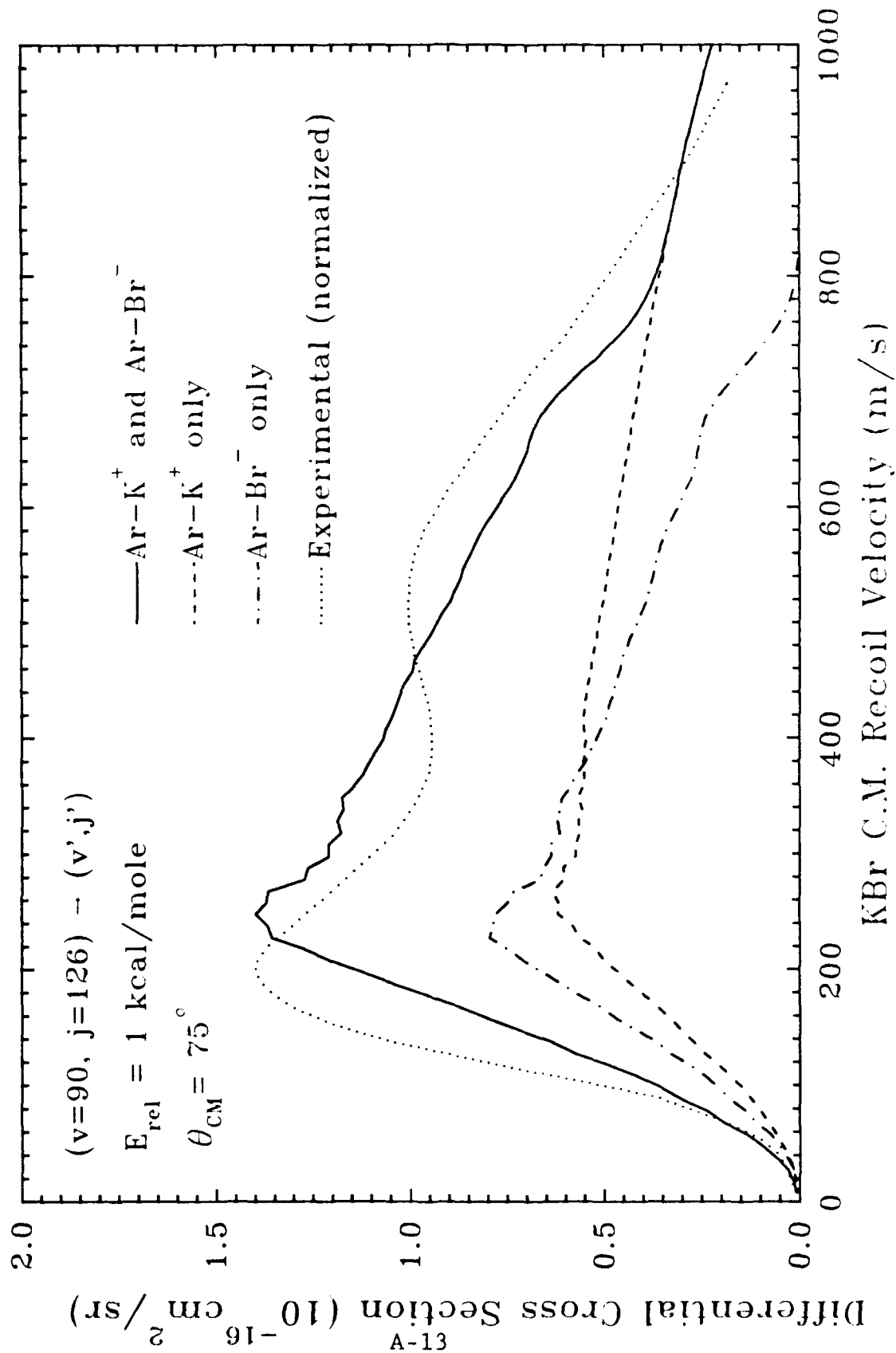
Figure 4
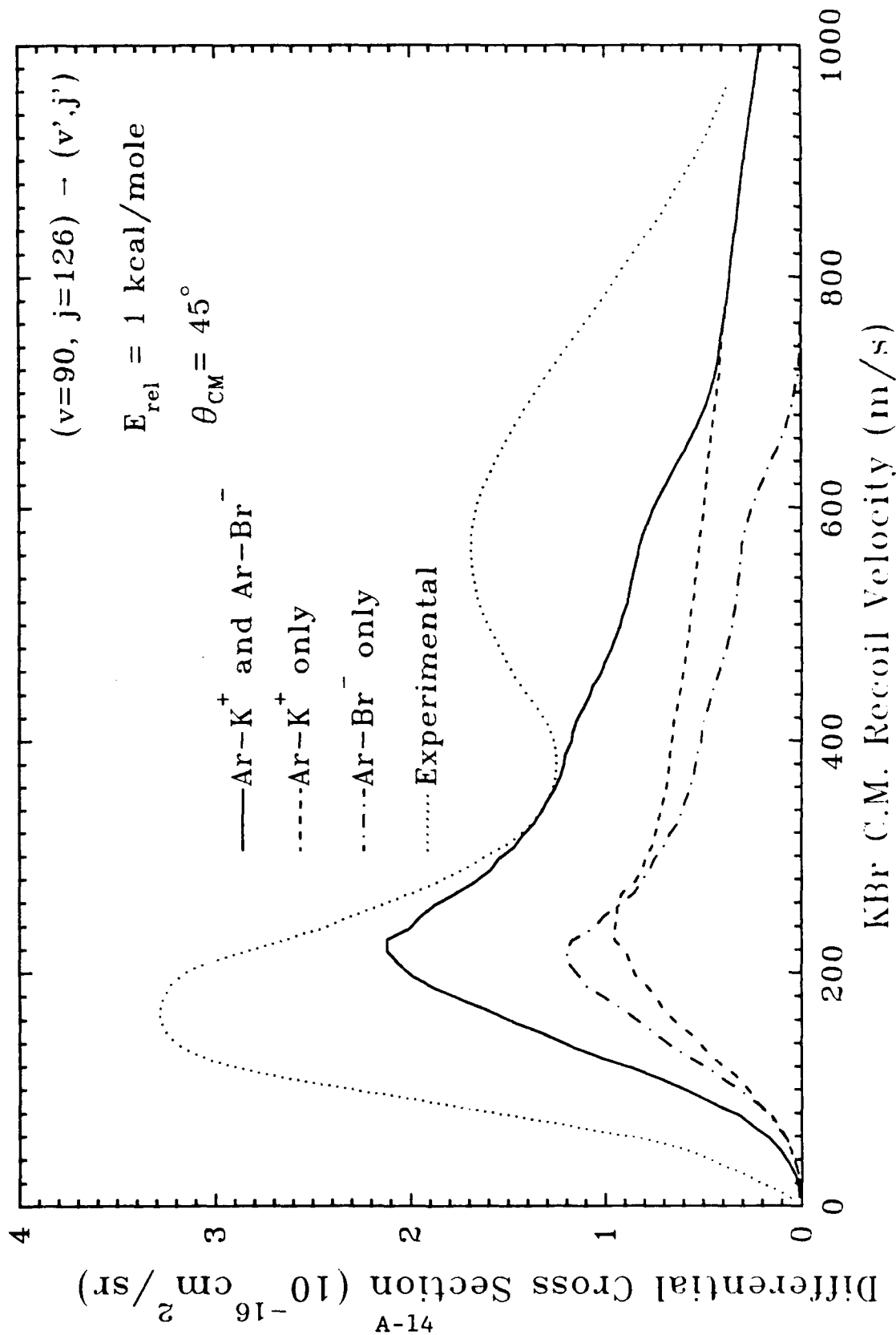
Differential Cross Section ($10^{-16}$cm$^2$/sr)

A-14

APPENDIX B

# MECHANISM OF BALLISTIC COLLISIONS. [*]

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## ABSTRACT

Ballistic collisions is a term used to describe atom-diatom collisions during which a substantial fraction of the initial relative translational energy is converted into the internal energy of the diatom. An exact formulation of the impulse approach to atom-diatom collisions is shown to be in excellent agreement with the experimental results for the CsF-Ar system at 1.1 eV relative translational energy for laboratory scattering angles of 30° and 60°. The differential cross section for scattering of CsF peaks at two distinct recoil velocities. The peak centered at the recoil velocity corresponding to elastic scattering has been called the elastic peak. This peak is shown to consist of several hundred inelastic transitions, most involving a small change in internal energy. The peak near the center-of-mass (c.m.) velocity is called the ballistic peak and is shown to consist of highly inelastic (ballistic) transitions. It is shown that transitions comprising the ballistic (elastic) peak occur when an Ar atom strikes the F (Cs) end of CsF. When one is looking along the direction of the c.m. velocity, the signal from a single transition which converts about 99.99 % of the relative translational energy into internal energy, may be larger than the signal from any other ballistic transition by as much as an order of magnitude. This property may be used to prepare state-selected and velocity-selected beams for further studies. It is also pointed out that the ballistic peak may be observed for any atom-molecule system under appropriate circumstances.

PACS NUMBERS: 34.80-i, 34.50.Bw, 34.50Gb

In a series of experiments, Herschbach and co-workers [1-3] have crossed a cesium halide (CsX) beam, at 90°, with an Ar beam at a relative translational energy of about 1 eV. The scattered CsX was plotted as a function of its recoil velocity in the laboratory frame for various laboratory scattering angles. In addition to the peak centered at where elastic scattering would be observed (elastic peak), another peak around the velocity corresponding to the center-of-mass (c.m.) motion was observed. It was established [1] that this peak arose from collisions during which a substantial fraction of the available translational energy had been converted into the internal motion of the diatom, and the name ballistic was attached to it. A ballistic peak was, however, not observed for the Ar-$I_2$ system.

Current theories of vibrational relaxation [4] are not able to account for the ballistic peak. A collinear (coplanar) classical model of atom-diatom collisions [5] predicts a large fractional energy transfer (~0.96) of the initial relative translational energy into vibrational (rotational) motion, $\Delta E/E \sim 0.96$, during a collision of Ar with CsF. It will be shown that when one is looking along or close to the direction of the c.m. velocity, transfer of 96% of the relative translational energy into internal energy does not lead to a ballistic effect. In addition, for the Ar-$I_2$ system this model *always* predicts a transfer of only ~25% of the relative translational energy into internal motion, whereas our calculation will be shown to predict a ballistic effect for this system at a relative translational energy of 0.122 eV.

In this letter we report a calculation of the ballistic phenomenon using a three-dimensional fully quantum exact impulse calculation [6] for the collision of CsF and $I_2$ with Ar. In the impulse calculations, the atom-diatom potential is represented by the sum of atom-atom potentials. Since the ground state of CsF is ionic, the $Cs^+$-Ar and $F^-$-Ar potentials are used to describe the CsF-Ar interaction. We neglect the long range part of the atom-ion potentials and approximate the short range repulsive potential by a hard core potential; the hard core $Cs^+$ ($F^-$) radii are approximated by Xe (Ne) radii,

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the numerical values being taken from Hirschfelder, Curtiss and Bird [7]. While this potential is expected to adequately describe the highly inelastic ballistic collisions, its description of near-elastic collisions at small c.m. scattering angles is incomplete [6]. This is because of the neglect of the attractive part of the interaction potential, which makes an important contribution to the small angle c.m. scattering , especially for near-elastic collisions. The elastic peak reported in the experiments under discussion [1-3] corresponds to c.m. scattering angles of 60°-175° and is therefore expected to be adequately described by the impulse calculation.

Normally, collisions resulting in large rotational excitation are believed to involve large c.m. scattering angles [8]. However, when almost all of the relative translational energy is converted into internal energy of the diatom, the final orbital angular momentum is almost zero and the scattering becomes nearly isotropic. Further, to conserve total angular momentum, all of the initial orbital angular momentum must appear as rotational angular momentum of the diatom. Suppose an Ar atom collides with a CsF molecule at a relative translational energy of 1 eV and almost all of the relative translational energy is converted into the internal energy of the diatom. In the impulse picture, a torque is exerted on the molecule and its rotational quantum number can change by up to $r_t \times p_3$, where $r_t$ is the distance between the atom of the diatom involved in the collision (non-spectator atom) and the c.m. of the diatom, and $p_3$ is the atom-diatom relative momentum. If Ar strikes the F end of CsF, the rotational quantum number of CsF may change by up to ~240. On the other hand, if Ar collides with the Cs end of CsF the rotational quantum number may change only by up to ~36. Since the greater change in rotational quantum number permits the conversion of a substantial fraction of the relative translational energy into the internal energy, a ballistic collision is possible during an encounter of Ar with the F end, and not with the Cs end, of CsF.

During a collision of Ar with $I_2$, at a 1 eV relative translational energy, the rotational quantum number may change by up to about 160. If the initial internal

excitation of $I_2$ is taken to be 250 °K ($v=0$ and $j=70$), to correspond to the source of the $I_2$ beam in the experiments [1-3], the final rotational quantum number may only be as high as 230. This would convert only 20% of the initial relative translational energy into rotational motion. For this reason the ballistic effect is not observed for Ar-$I_2$ collisions under the conditions described above. If, however, the $I_2$ beam is heated to 1000 °K or a heated CsI beam is substituted for $I_2$, higher rotational levels become available and permit, for the same amount of torque, the conversion of about half of the 1 eV initial relative translational energy into internal energy in a single encounter, and the ballistic effect may be possible during a subsequent encounter with the other end of the molecule.

The equations used to calculate the c.m. differential cross section using the impulse formalism (IA) were given earlier [6] and will not be repeated here. Most of the cross sections used here were computed using a semiclassical approximation to the exact IA calculation developed earlier [6]. A spot check of semiclassical cross sections showed a deviation from the exact cross sections by no more than 10%.

The laboratory and c.m. differential cross sections for transitions between different vibrational-rotational states are related by:

$$\left(\frac{d\sigma}{d\Omega}\right)_L = \left(\frac{d\sigma}{d\Omega}\right)_{CM} \frac{\int_{\Omega_m}^{\Omega_M} d\Omega_{CM}}{\Delta\Omega_L}, \qquad (1)$$

where $\Omega_L$ is the laboratory solid angle; $\Omega_M$ and $\Omega_m$ are the c.m. solid angles corresponding to laboratory scattering angles $\Omega_L \pm \Delta\Omega_L/2$. We have assumed the c.m. differential cross-section does not vary significantly with the c.m. scattering angle. The error introduced by this assumption is a few percent. The factor multiplying $(d\sigma/d\Omega)_{c.m.}$ on the R.H.S. of Eq. (1) is the Jacobian for the transformation of the differential cross-section from the c.m. to the laboratory coordinate system, usually written as $(v_L/u)^2$, u and $v_L$ being the recoil velocities of CsF in the c.m. and

laboratory coordinate systems, respectively. The Jacobian, as seen from Eq. (1), also determines the c.m. solid angle seen via $\Delta\Omega_L$, the laboratory solid angle. As the ratio $u/v_L$ becomes smaller, larger c.m. solid angles become accessible for a given $\Delta\Omega_L$ until the whole $4\pi$ steradians scatter into it. After this the Jacobian becomes constant. The consequence of this is that $(d\sigma/d\Omega)_L$ does not become infinite as u approaches zero.

Calculated $(d\sigma/d\Omega)_L$ as a function of laboratory recoil velocity of CsF is plotted in Fig. (1) for a relative translational energy of 1.1 eV at laboratory scattering angles of 30 and 60 degrees. Two peaks are clearly seen for scattering at 60°, a ballistic peak around 550 m/s and an elastic peak near 1050 m/s, in agreement with the experiments [1-3]. The resolution of the detector is wider for larger velocities. It therefore records the true values 662 m/s and 1194 m/s for the ballistic and elastic peaks at the smaller values cited above. For 30° scattering, the two peaks merge. The calculation is in excellent agreement with the experimental observations for both scattering angles.

Figure (2) gives a discrete plot of the differential cross section for the elastic and ballistic transitions as a function of the laboratory recoil velocity of CsF for laboratory scattering angles of 30°, 53.3° (direction of c.m. velocity) and 60°. The initial vibrational-rotational level of CsF is $v=0, j=70$; other beam parameters are the same as in figure (1). Separate peaks for scattering from the Cs end and the F end of CsF are clearly seen. Scattering from the Cs end, called the elastic peak, is very similar in all three cases. The final rotational levels are roughly bound by the available torque and are limited to $|\Delta j| \sim 50$. The scattering from the F end (ballistic scattering) produces the largest change in rotational quantum numbers when the CsF recoil velocity equals the c.m. velocity (662 m/s). On either side of the ballistic peak the final rotational quantum number decreases. For 53.3° and 60° scattering, the cross section decreases monotonically and the magnitude of the laboratory cross section is determined primarily by the Jacobian of transformation from the c.m. to the laboratory

system. All of the fifteen most probable ballistic transitions for these two scattering angles had $\Delta E/E$ greater than 0.97. The ballistic effect would not be observed at these angles if none of the transitions transferred more than 96% of the relative translational energy into internal energy. For 30° scattering the differential cross section shows a dip and an increase before going to zero as we move away from the c.m. velocity. On the left side of the c.m. velocity, the dip at the CsF recoil velocity of about 470 m/s is a reflection of the small inelastic scattering cross section for small c.m. scattering angles. On the right side the increase in the differential cross section following the dip at the CsF recoil velocity of about 800 m/s is a reflection of the rotational rainbow. For the two larger scattering angles the rotational rainbow is not seen. In all cases the large laboratory cross sections near the c.m. velocity arise solely due to the transformation from the c.m. to the laboratory frame. When viewing along the direction of the c.m. velocity (53.3°), the ballistic effect acquires special significance. One transition has a much larger cross section than any other transition. In the figure, the two tallest lines denote the transition to the final state $v'=2$, $j'=231$, $\Delta E/E= 0.9997$, which has a cross section larger by a factor of about 3 than any other transition. This fact can be used to separate this final state from other final states and prepare state-selected and velocity-selected beams.

Impulse calculations were also carried out for the $I_2$-Ar system for a 250 °K $I_2$ beam at relative translational energies of 1 eV and 0.122 eV. At the larger relative translational energy the ballistic effect was not obtained, in agreement with the experimental observations. For the smaller relative translational energy, figure 3, one ballistic transition to $I_2(v'=0,j'=258)$, $\Delta E/E=0.9990$, imbedded in a sea of inelastic transitions, is clearly seen. It is also seen from this figure that the next most probable transition, to $I_2(v'=0,j'=256)$, $\Delta E/E = 0.9605$, has an order of magnitude smaller cross section. The c.m. differential cross section divided by the c.m. final velocity, i.e., the c.m. differential cross section without the density of states factor, for the two

transitions differs by less than 3%. Again, it is the Jacobian of transformation to the laboratory frame that makes the resonant T→R transition ballistic. A calculation for the Ar-CsI system (CsI beam temperature 1000°K, relative translational energy = 1eV) failed to give a ballistic peak, in contrast to the experiments [1] which observed a ballistic peak under the above conditions. The two ends of the diatom have similar masses and the possibility, mentioned earlier, that the double collision terms lead to the ballistic effect is being investigated.

In summary, we have constructed a model of ballistic phenomenon using the three dimensional fully quantum impulse approach to atom-diatom collisions. This model has given an explanation of the ballistic and elastic peaks observed in the Ar-CsF experiment and has predicted ballistic transitions for the $I_2$-Ar system at a relative translational energy of 0.12 eV. The model, however, needs extension to explain the Ar-CsI results. This model has not used any properties specific to CsF or $I_2$. Therefore, the most important result of this study is that the ballistic effect should be observable for every atom-molecule system under suitable conditions. In addition, our model makes several predictions, e.g., (i) the population of very high rotational levels during the ballistic collisions of CsF or $I_2$ with Ar, and, (ii) the ballistic peak has fewer transitions, and a single transition may have a substantially larger differential cross section than any other transition, for the correct viewing geometry. The last prediction of our model has important consequences in that the ballistic effect may be used to prepare state-selected and velocity-selected diatom beams for further studies.

# FIGURE CAPTIONS

Figure (1). The differential cross section for the scattering of CsF by Ar at a relative translational energy of 1.1 eV for the vibrational-rotational states $v=0, j=70$ (small dashed line), $v=1, j=35$ (long dashed line) and $v=2, j=70$ (dotted line), summed over all the final states, versus the laboratory recoil velocity of CsF at laboratory scattering angles of 30.0° and 60.0° with an angular resolution of $\pm0.125°$. The resolution of the instrument was taken into account by scanning a normalized Gaussian function with full width at half-height given by Eq. (1) of Ref. (1) over the calculated cross sections to obtain the curves plotted in the figure. The distortion caused by the instrumental resolution accounts for the discrepancy between the 0.73 eV relative translational energy reported earlier [3] and 1.1 eV given by us. The experimental data are normalized to match the point having the largest measured cross section with the calculation for the $v=0, j=70$ initial state.

Figure (2). Discrete plot of the state-to-state differential cross sections as a function of recoil velocity for a collision of CsF ($v=0, j=70$) with Ar at a relative translational energy of 1.1 eV for laboratory scattering angles of 30°, 53.3° and 60°. The velocities of the Ar and CsF beams are 2550 m/s and 500 m/s, respectively, and the angle of the centroid velocity is 53.3°. Two distinct scattering regions are clearly seen, one corresponding to scattering from F (ballistic peak) around the c.m. velocity (662 m/s) and one due to scattering from Cs (elastic peak) near 1050 m/s.

Figure (3). Discrete plot of the state-to-state differential cross sections as a function of recoil velocity for a collision of $I_2$ with Ar. The angle of the centroid velocity is 32.2° and the lab scattering angle is $32.2\pm.125°$. Two ballistic peaks corresponding to the final state $v'=0$, $j'=258$, each having a cross section about an order of magnitude larger than the other transitions, are clearly seen.

## REFERENCES

1. H.J. Loesch and D.R. Herschenbach, "Ballistic Mechanism for Vibrational and Rotational Energy Transfer in Ar + CsI Collisions," J. Chem. Phys., 57: 2038 (1972).

2. D.L. King, H.J. Loesch and D.R. Herschenbach, Discuss. Faraday Soc., 55: II-34 (1973).

3. D.L. King, Ph.D. Thesis, Chemistry Department, Harvard University, 1974.

4. R.D. Levine and R. B. Bernstein,, Molecular Reaction Dynamics 2nd ed., Oxford University Press, New York, 1987.

5. S.W. Benson, G.C. Berend and James C. Wu, "Classical Model for Vibrational and Rotational Excitation of Diatomic Molecules by Collision," J. Chem. Phys. 38: 25 (1963). See also S.W. Benson, The Foundations of Chemical Kinetics, McGraw-Hill Book Co., New York, 1960.

6. R.D. Sharma, P.M. Bakshi and J. M. Sindoni, "Impulse Formalism for Atom-Diatom Collisions," Phys. Rev. A 43: 189 (1991). R.D. Sharma and J.M. Sindoni, "Relaxation of Highly Vibrationally Excited KBr by Ar," Phys.Rev. A 45: 531 (1992).

7. J. O. Hirschenfelder, C.f. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, 1954. The hard core radii used were: $r(Ar-Cs^+)=3.5$ A, $r(Ar-F^-)=3.1$ A and $r(Ar-I)=2.96$ A.

9. Molecular Collision Dynamics edited by J. M. Bowman, Springer Verlag, New York, 1983, Chapt. 4.

Figure 1

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Figure 2

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$\Delta\epsilon/E_{rel}$

$V_{Ar} = 800$ m/s $(90^{\circ})$

$V_{I_2} = 200$ m/s $(0^{\circ})$

$E_{rel}=0.1217$eV $\quad p_3=44.8\times10^8$ cm$^{-1}$

$(v=0, j=200) \rightarrow (v',j')$

$(v'=0, j'=258)$

$v'=0$

$v'=1$

$v'=2$

$v'=3$
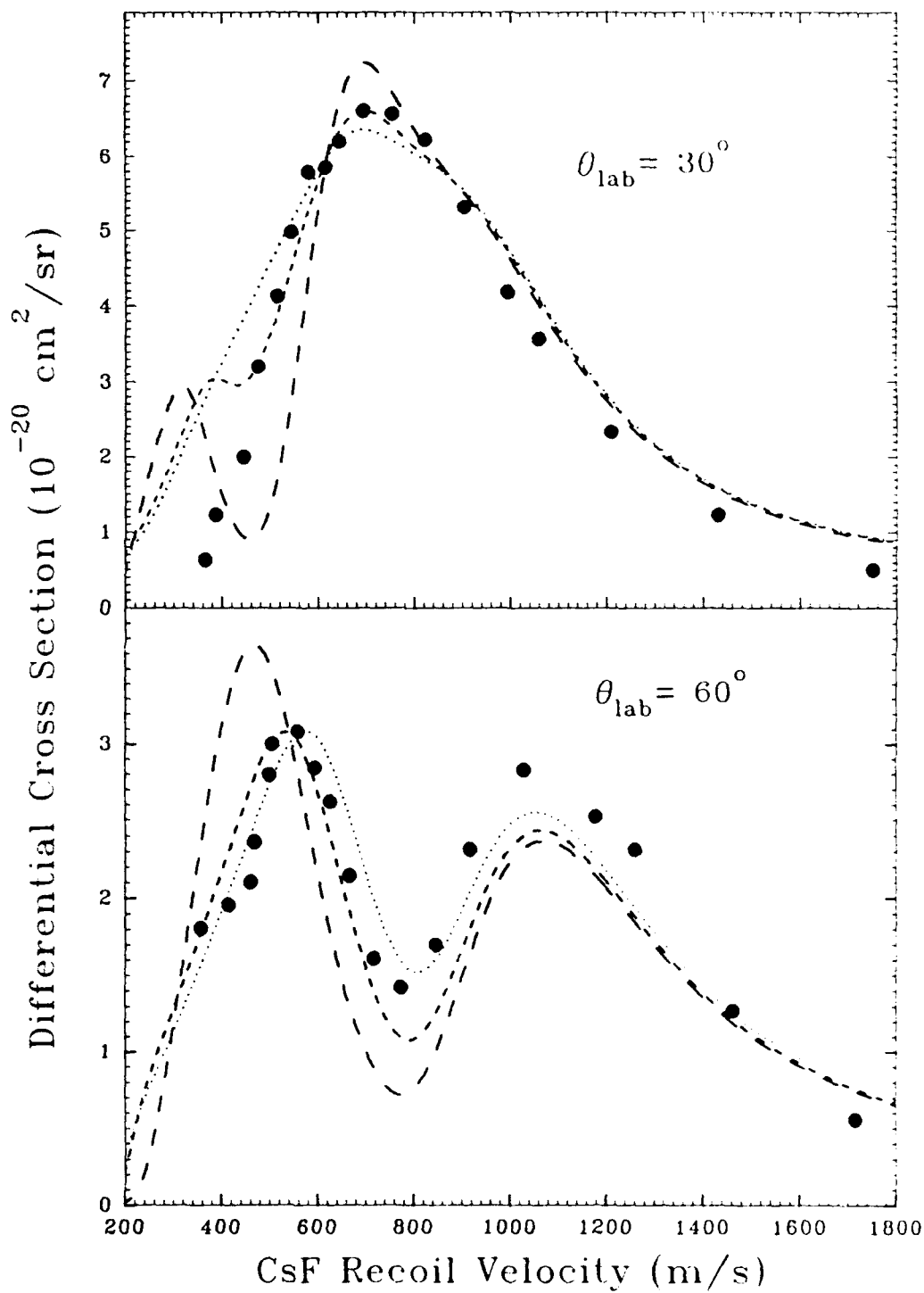
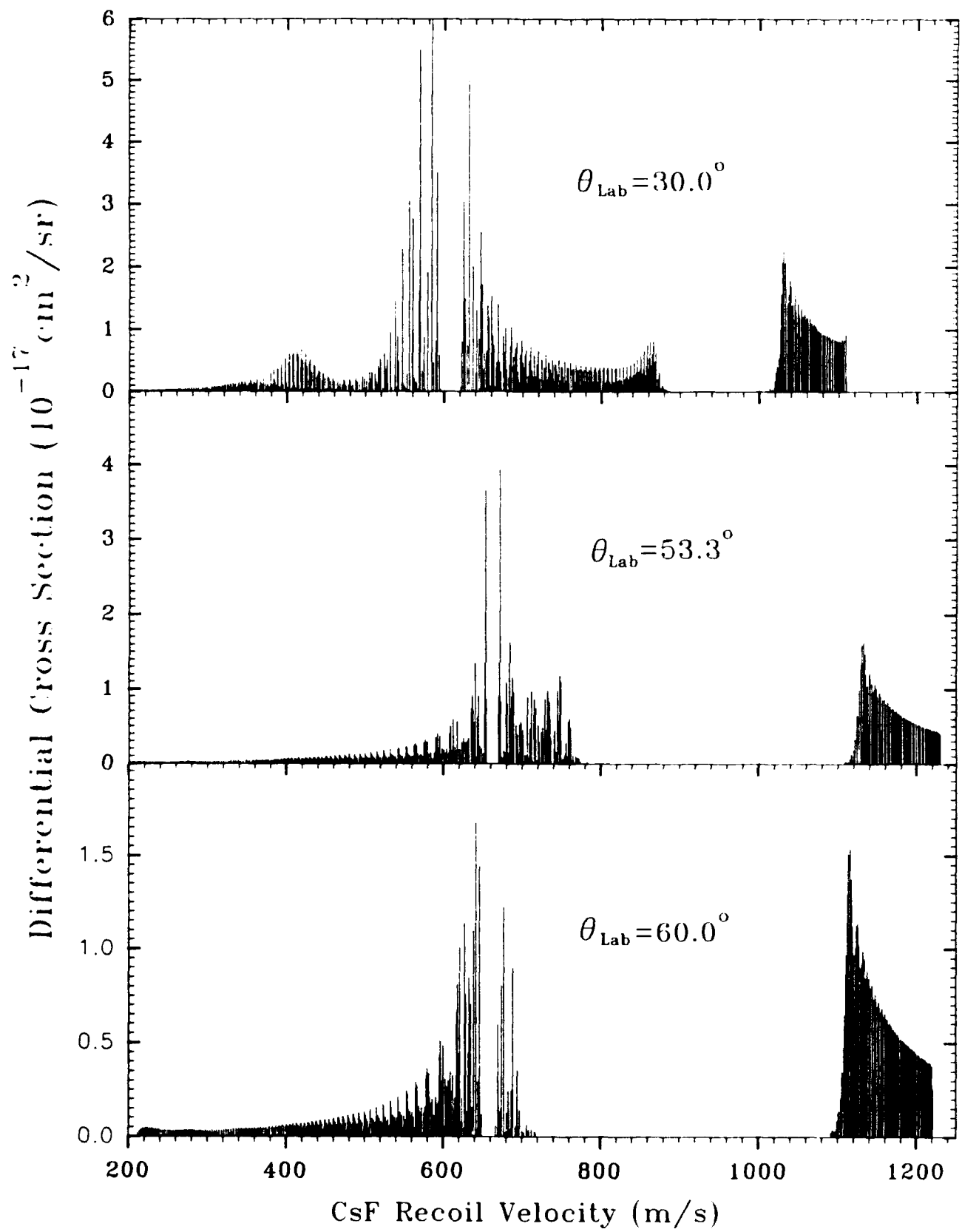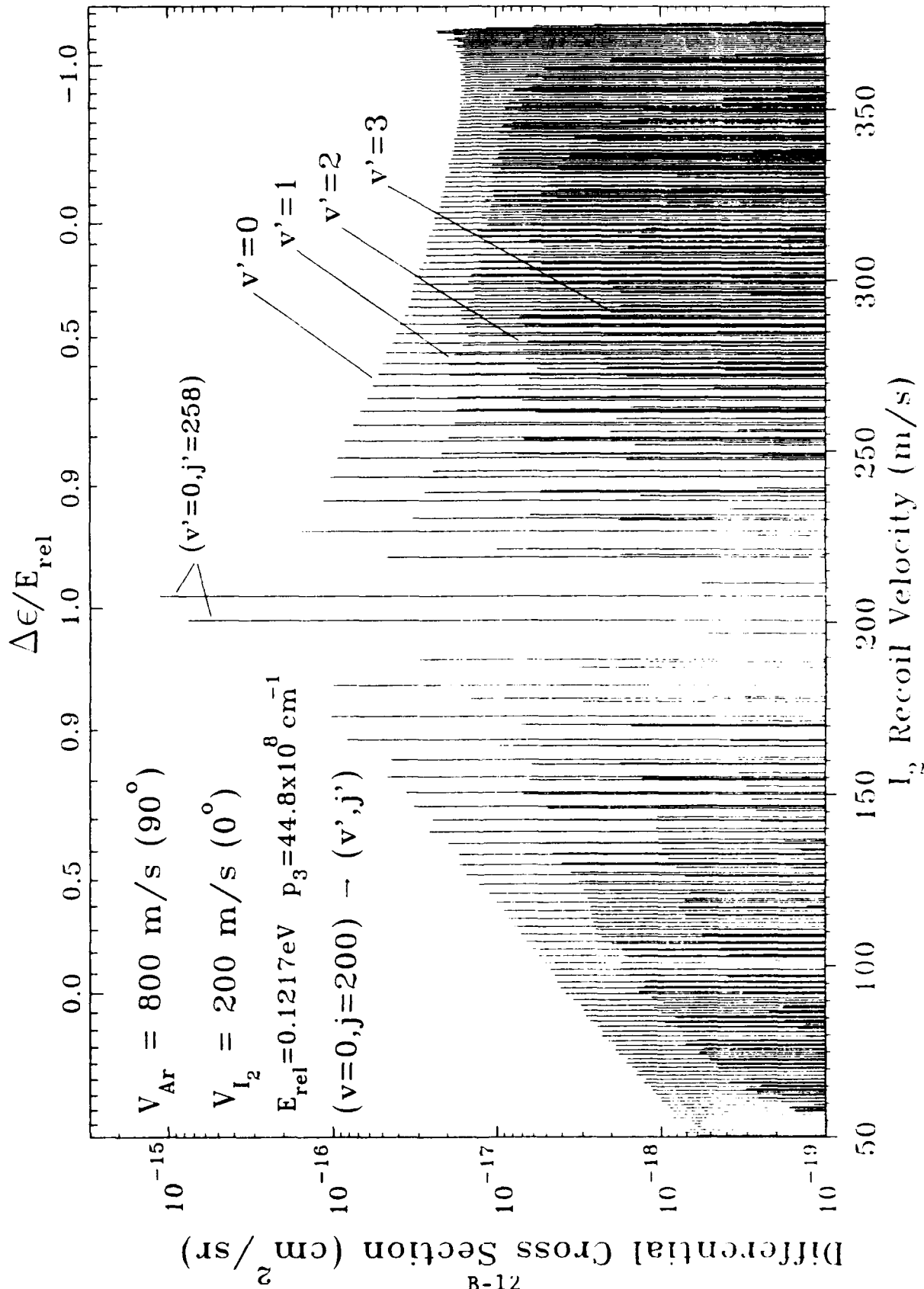Differential Cross Section (cm$^2$/sr)

$I_2$ Recoil Velocity (m/s)

Figure 3

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APPENDIX C

A Proposal to Produce Velocity-Selected and State-Selected Molecular Beams
Using The Ballistic Effect. *

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Ma.01730

The study of chemical reactions and energy transfer processes using molecular beams has revolutionized our understanding of the mechanisms underlying these processes[1]. Still, except for a few fortunate instances[2], most of the processes studied involve reactants with low internal excitation[3] or with Boltzmann distributions at the oven temperature[4-6]. In this letter we propose a method for producing molecule beams in a desired internal state and travelling with a desired velocity. The rates of chemical reactions are known to depend, sometimes strongly, upon the initial state of the reactants. One should expect greatly improved understanding of the chemical reactions and the possibility of studying many more reactions using the ideas presented here. We illustrate the method by describing the circumstances leading to the production of a desired $N_2$ beam resulting from collisions of $N_2$ with $Li^+$ in crossed beams - a system studied extensively by Toennies and co-workers[3].

The method is based upon the ballistic effect discovered about 19 years ago[4-6]. Herschbach and co-workers studied the collisions between an alkali halide molecule and an Ar atom at about 1 eV relative translational energy by crossing two beams and measuring the laboratory recoil velocity of the alkali halide molecule as a function of the laboratory scattering angle. In addition to a peak centered at the recoil velocity of elastically scattered alkali halide molecules (pseudoelastic peak, formerly called elastic peak[7]), another equally strong peak centered at the recoil velocity corresponding to the motion of the center-of-mass (ballistic peak) was observed. Obviously, the ballistic peak is contributed to only by those alkali halide molecules which are almost stationary

in the center-of-mass (c.m.) frame and have nearly all of the collision (relative translational) energy converted into the internal (vibrational and/or rotational) energy.

A theory of ballistic collisions[8] gives excellent agreement with the measured results for the CsF-Ar system at the laboratory scattering angles of 30 and 60 degrees. According to this theory, when the differential cross section for the scattering of alkali halide molecules is measured along the direction of the c.m. velocity, only a few transitions contribute to the ballistic peak. This is in contrast to several hundred inelastic transitions making up the pseudoelastic peak. Further, when the relative translational energy equals the energy of one of the rotation-vibration transitions (resonant T-(V,R) process), this transition may have a differential cross section which is larger than that of any other neighboring transition by as much as an order of magnitude. This gives us a state-selected beam travelling at the speed of the c.m. It should be pointed out that the differential cross section of the resonant transitions in the c.m. frame is nearly equal to the nearby nonresonant transitions. The resonant transition has a much larger differential cross section in the laboratory frame because of a greater Jacobian of transformation from the c.m. to the laboratory coordinates. Physically it means that, for the correct viewing geometry, the signal from the entire 4pi steradian solid angle in the c.m. frame may be collected by a small solid angle in the laboratory frame.

The differential cross sections are calculated using an exact formulation of a three-dimensional quantum-mechanical impulse approach (IA) calculation described earlier[9]. Physically, one may use the impulse calculation when the time duration of the collision is much shorter than the periods of vibrational and rotational motion of the diatom. The nuclei constituting the diatom may then be considered stationary during the collision and the intramolecular potential is the generator of the momentum distribution of the constituent nuclei. The atom-molecule potential, in the IA, is written as the sum of the atom-atom potentials and the atom-atom scattering amplitudes are added to

obtain the atom-molecule scattering amplitudes. The atom-atom potential, in the present study, is described by a hard core interaction. Following the previous study[9], the hard core radius for the $Li^+$-N interaction is taken to be 1.62 Å.

Figure 1 is a plot of the calculated laboratory differential cross section for the excitation of $N_2(v=0,j=0)$ during a collision with $Li^+$, with a relative translational energy of 0.8825 eV, as a function of the laboratory recoil velocity at the laboratory scattering angle of 48.0($\pm$0.125) degrees. A beam of $N_2$ molecules in the state $v=3$, $j=10$ travelling at 1440 m/s may be obtained by filtering out velocities lower than 1350 and higher than 1550 m/s. The character of ballistic scattering in this calculation is qualitatively different from that in the previous work[8] where, when the scattering is viewed along the c.m. velocity, several ballistic transitions are calculated although one transition is still dominant. For the $Li^+$-$N_2$ system there is only one ballistic transition.

Because of the small rotational constant and low frequency of the vibration of the diatomic molecules studied in the earlier work[8], several rotation-vibration transitions could be nearly-resonant (DE/E-1) and appear ballistic. Because of the large rotational constant and high vibrational frequency of $N_2$ only one transition can be nearly-resonant. It is seen from figure 1 that if one interested in defining only the vibrational level, one may obtain a beam of $N_2$ molecules in $v=3$ by filtering out molecules with recoil velocities below 920 and higher than 1750 m/s. It should be noted, however, that defining only the vibrational level leads to an increase of signal by only a factor of about 2. Figure (2) demonstrates the feasibility of producing velocity-selected $N_2$ beams in the $v=6,j=0$ state. Lower values of the recoil velocities in the figures correspond to small c.m. scattering angles, resulting in transitions to only a few rotational levels having small quantum numbers. The transitions to different vibrational levels are well separated. Large values of recoil velocities, on the other hand, correspond to large c.m. scattering angles leading to large changes in the rotational

quantum number during the collision. The rotational transitions are therefore not as neatly bunched within each vibrational level.

A beam containing molecules in nearly any final state may be prepared by giving the appropriate energy to the collision partners provided the c.m. cross section for the particular transition is not too small ($<10^{-22}$ cm$^2$/sr). The velocity of the beam is equal to the c.m. velocity of the collision partners. The possibilities are limitless.

# REFERENCES

1.  R.D. Levine and R.B. Berstein, <u>Molecular Reaction Dynamics</u>, 2nd ed., Oxford University Press, New York, 1987.

2.  F.F. Crim, M.S. Chou and G.A. Fisk, "Inelastic Scattering of Vibrationally Excited KBr by Small Polar Molecules," <u>Chem. Phys.</u>, 65:733 (1976).

3.  R.Bottner, U. Ross and J. Peter Toennies, "Measurements of Rotational and Vibrational Quantum Transition Probabilities in the Scattering of Li+ from $N_2$ and CO at Center of Mass Energies of 4.23 and 7.07 eV," <u>J. Chem. Phys.</u>, 65 733 (1976).

4.  H.J. Loesch and D.R. Herschenbach, "Ballistic Mechanism for Vibrational and Rotational Energy Transfer in Ar + CsI Collisions," <u>J.Chem. Phys.</u>, 57:2038 (1972).

5.  D.L. King, H.J. Loesch and D.R. Herschenbach, <u>Discuss. Faraday Soc.</u>, 55: II-34 (1973).

6.  D.L. King, Ph.D. Thesis, Chemistry Department, Harvard University, 1974.

7.  Elastic peak was so named because it has the maximum intensity where one would detect the elastically scattered alkali halide molecules. This peak was later shown[8] to consist mainly of inelastically scattered alkali halide molecules. This was causing some confusion. At the suggestion of Dudley Herschenbach the elastic peak was renamed pseudoelastic peak. The new name is very appropriate because it describes the location of the peak and carries the warning label.

8.  R.D. Sharma, P.M. Bakshi and J.M. Sindoni, "Mechanism of Ballistic Collisions," <u>Phys. Rev. A</u>, 43: 189 (1991).

9.  R.D. Sharma, P,M. Bakshi and J.M. Sindoni, "Impulse Formalism for Atom-Diatom Collisions," <u>Phys. Rev. A</u>, 43: 189 (1991).

FIGURE CAPTIONS

Figure 1. Differential Cross Section ($cm^2/sr$) in the laboratory frame for the scattering of $N_2$(initial state v=0,j=0) upon colliding with $Li^+$ with a relative translational energy of 0.8825 eV as a function of the laboratory recoil velocity of $N_2$ at the laboratory scattering angle (48°±0.125°) coincident with the direction of the c.m. velocity vector (48.3°). The lone ballistic transition to the final state of $N_2$(v'=3,j'=10), DE/E= 0.99987, can be clearly seen.

Figure 2. Differential Cross Section ($cm^2/sr$) in the laboratory frame for the scattering of $N_2$(initial state v=0,j=0) upon colliding with $Li^+$ with a relative translational energy of 1.68 eV as a function of the laboratory recoil velocity of $N_2$ at the laboratory scattering angle (57.5°±0.125°) coincident with the direction of the c.m. velocity vector (57.46°). The lone ballistic transition to the final state of $N_2$(v'=6,j'=0), DE/E= 0.99994, can be clearly seen.

# A Proposal to Produce Velocity-Selected and State-selected Molecular Beams Using The Ballistic Effect.

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## ABSTRACT

Theory of ballistic collisions is used to propose a method for the production of velocity-selected and state-selected molecular beams. The method is illustrated by describing the circumstances leading to the production of a desired $N_2$ beam resulting from collisions of $N_2$ with $Li^+$ in crossed beams.

Fig. 1

Differential Cross Section (cm²/sr) vs N₂ Recoil Velocity (m/s)

v'=0, v'=1, v'=2, v'=3, (v'=3,j'=10)

Fig. 2

v'=0, v'=1, v'=2, v'=3, v'=4, v'=5, (v'=6,j'=0)