Collinear reactive scattering of state-selected $H_2^+ + He \rightarrow HeH^+ + H$: A method for probing dynamical resonances

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The detection of dynamical resonances in reactive scattering continues to elude experimentalists, despite tremendous effort. Theory predicts that for specific reactant energies and orientations, energy can become momentarily trapped in bound vibrational or rotational states of an otherwise dissociative collision complex. The quasibound states can persist long enough to influence the product scattering angle, internal state distribution, or reaction probability.[1,2] These resonances, which represent the "transition states" of the reactive complex, provide a critical test of quantum mechanical formulations of reaction dynamics. Neumark *et al.* reported crossed molecular beam scattering measurements of the reaction $F + H_2 \rightarrow HF + H$ which show some characteristics of scattering resonances, but the interpretation has been debated and data are available at only a few collision energies.[3] Nieh and Valentini observed apparent resonances in the state-selected integral cross section for the reaction $H + H_2 \rightarrow H_2 + H$.[4] These results are intriguing because the experiment, conducted under "bulb" conditions, presumably averaged over scattering angles and impact parameters. However, subsequent theoretical[5,6] and experimental[7] evidence suggests that the observed collision-energy dependent structure is due to some other, as yet unidentified, process.

We report on an experimental scattering and detection geometry for studying dynamical resonances in bimolecular collisions. State-selected differential cross sections are measured at center-of-mass (c.m.) scattering angles $\theta = 0°$ and 180° for the reaction $H_2^+(v = 0,1,2; j = 1) + He \rightarrow HeH^+ + H$ as a near-continuous function of the collision energy. Previous experiments aimed at detecting resonance effects in state-selected differential cross sections did not scan over collision energy.[3,8,9] Experiments that have scanned collision energy only measured the integral cross sections.[4,7,10,11] The present technique offers a unique combination of reactant state selectivity, collision energy resolution, and product scattering-angle detection, which improves the prospect of detecting scattering resonances. Near the reaction threshold, the product flux at $\theta = 180°$ (relative to the direction of the incident He) is due mainly to low angular momentum and low impact parameter collisions corresponding to the collinear coordinate.

The scattering geometry illustrated in Fig. 1 introduces three important experimental conditions.

(1) The reactant relative velocity vector lies along a nearly fixed laboratory axis for all collision energies. This allows the detector to view the c.m. scattering angles $\theta = 0°$ and 180° using a single laboratory angle.

(2) HeH^+ product velocity measurements distinguish "rebound" reactions scattered at $\theta = 180°$ from "stripping" reactions at $\theta = 0°$

(3) Vibrationally state-selected $H_2^+(v, j)$ is produced with little rotational angular momentum (almost entirely $j = 1$) by resonance-enhanced multiphoton ionization.

Ideally, one would like to measure differential cross-sections with complete quantum state resolution of the reactant $H_2^+(v, j)$ and product $HeH^+(v', j')$. Because collinear reactions essentially conserve j for low-j (i.e., $j' \simeq j$), the use of reactant state preparation and product detection at $\theta = 180°$ approaches a state-to-state differential scattering measurement.

In a classical picture (assuming direct scattering), product observed at a given θ receives contributions from a range of values of b (impact parameter), j (rotational angular momentum), and χ (rotational phase or orientation.[2,12] Reactions due to nonrotating collinear collisions ($b = j = \chi = 0$) lead to product at $\theta = 180°$. These conditions are strongly favored in our experiment because rebound scattering at $\theta = 180°$ occurs only for small values of b (peaked at $b = 0$) and because state-selected H_2^+ is produced with little rotational energy. These constraints limit the detection of product at $\theta = 180°$ to low-j collinear oriented reactions ($\chi \simeq 0°$). For indirect (resonance) reactions, the width of the scattering angle distribution $\Delta\theta$ for a particular set of b, j, and χ values increases with resonance lifetime.[6] However, because $\Delta\theta$ is proportional to the total angular momentum J of the complex, indirect

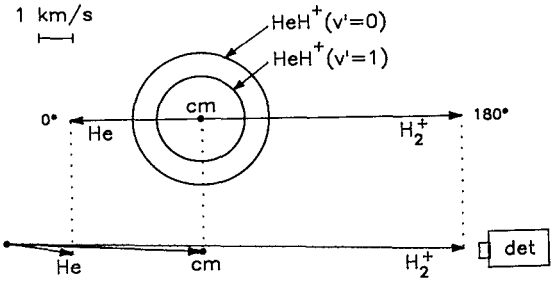

FIG. 1. Newton diagram for $H_2^+(v) + He \rightarrow HeH^+(v') + H$ showing the velocity vectors in the laboratory frame and c.m. frame (the c.m. vectors are displaced for clarity). This example corresponds to $v = 2$ and $E_c = 0.9$ eV. The reactant He velocity vector defines the c.m. scattering angle $\theta = 0°$. The quadrupole mass spectrometer detector views the c.m. scattering angles $\theta = 0°$ and 180°, independent of collision energy.

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scattering is not expected to have an adverse affect on the detection of collinear reactions for which $J \simeq 0$. The selectivity of the experiment is further enhanced at energies near threshold because (1) collinear collisions maximize the component of the relative velocity directed along the reaction coordinate (thereby avoiding a centrifugal barrier), and (2) the reaction threshold increases away from the collinear geometry[13] (this steric effect also holds for $H + H_2$[14]).

A full description of the experiment will be given in a future publication.[15] Briefly, a 3:1 He/H_2 mixture expands through a 0.5 mm diam pulsed nozzle and passes through a skimmer and collimator to form a 5 mm diam beam at the ionization region. State-selected $H_2^+(v,j)$ ions are produced by 3 + 1 REMPI through the H_2 $\tilde{C}\,^1\Pi_u$ ($v = 0,1,2$) $Q(1)$ transitions.[16] The vibrational purity of the ions formed by this method has been previously measured to be the following: For $\tilde{C}(v=0)$ excitation [91% ($v=0$), 9% ($v=1$)]; for $\tilde{C}(v=1)$ excitation [7% ($v=0$), 74% ($v=1$), 15% ($v=2$)]; for $\tilde{C}(v=2)$ excitation [14% ($v=1$), 59% ($v=2$), 21% ($v=3$)].[17] The ion rotational state distribution consists entirely of $j=1$ and $j=3$, in the ratio 10:1 at $\tilde{C}(v=0)$, 4:1 at $\tilde{C}(v=1)$, and 2:1 at $\tilde{C}(v=2)$.[17] Photoions are accelerated near-coaxially to the neutral beam by applying a 10 ns pulsed electric field; the short duration ensures that ions reach the desired collision energy in a distance much smaller than the scattering path length.[16] The typical energy spread due to reactant ion space-charge repulsion is $\Delta E_c = 0.15$ eV FWHM. The scattering length is controlled by tilting the ion beam and detector axis 2° away from the neutral beam; the resulting product ion velocity resolution $\Delta v/v \simeq 0.08$ is sufficient to distinguish forward and backward scattered HeH^+ but does not resolve the $(v'j')$ state distribution. Examples of HeH^+ Cartesian flux[18] vs c.m. velocity for a collision energy of $E_c = 0.9$ eV are shown in Fig. 2 for different H_2^+ vibrational states.

The differential cross section for c.m. scattering angle $\theta = 180°$ is presented as a function of collision energy E_c in Fig. 3 for the nominal states H_2^+ ($v = 0,1,2; j = 1$). The quantity measured is $d\sigma/d\omega(\theta = 180°)$,[15] which we interpret here as reaction probability $P_{v,j}(\theta = 180°)$. Although the final vibrational state v' is not resolved, only the $v' = 0$ channel is open for energies < 0.4 eV above the reaction threshold. The results in Fig. 3 are consistent with calculated[13,19–22] and observed [11,23] values for the reaction thresholds, vibrational enhancements, and relative magnitude of the cross sections.

The reaction $H_2^+ + He \rightarrow HeH^+ + H$ is 0.81 eV endothermic, and the potential exhibits a well depth of about 0.25 eV for linear $[H_2^+\text{–He}]$.[22] Recently Kress *et al.*[19] and Zhang *et al.*[20] using somewhat different potential surfaces, published 3D quantum calculations for $H_2^+ + He$ at $J = 0$. Both groups calculated state-selected reaction probabilities which show numerous oscillations as a function of collision energy. The resonance structure is particularly dense due to the well in the entrance channel, which supports many closely spaced states.[24] The calculated resonance structure for $H + H_2$, by contrast, is broader and less congested.[5] 2D

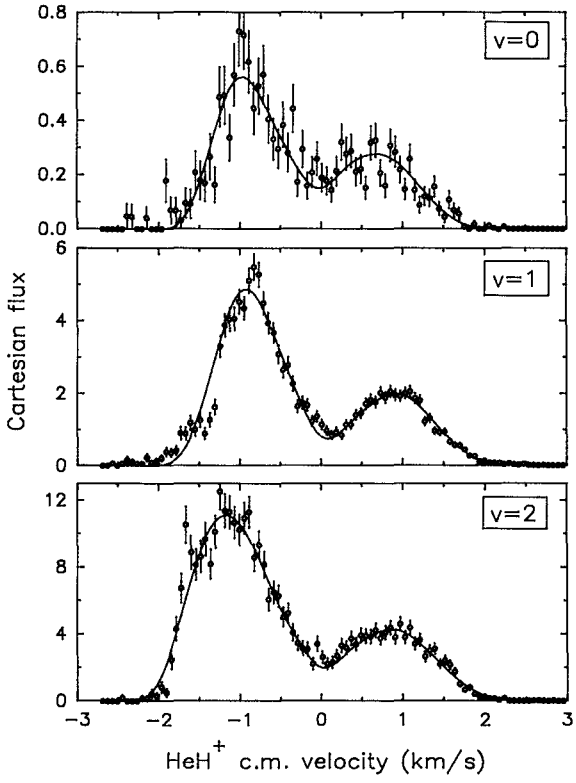

FIG. 2. Cartesian flux vs HeH^+ c.m. velocity for $H_2^+ + He \rightarrow HeH^+ + H$ at $E_c = 0.9$ eV. The ($\theta = 180°$) and ($\theta = 0°$) components are labeled by positive and negative velocity, respectively. The calculated curve is a best-fit to the data points using a forward-convolution algorithm (Ref. 15). All plots use the same relative flux units to show the observed increase in signal with H_2^+ vibrational excitation. The vibrational purity of H_2^+ (v) is given in the text.

quantum mechanical scattering calculations for the collinear coordinate also show many narrow resonances in the $H_2^+ + He$ reaction probabilities.[21,22]

The data in Fig. 3 show undulations that may be residual structure from instrumental broadening of a complicated resonance spectrum. Although each data set is the sum of many energy scans, it remains difficult to discern real features because of the low count rate. The experimental collision energy resolution of $\Delta E_c = 0.15$ eV compares favorably with previous cross section measurements. Kliner *et al.* report $\Delta E_c = 0.3$ eV for a state-to-state integral cross section measurement of $H + H_2$ under bulb conditions.[7] They assert that the same resolution applies to the results of Nieh and Valentini.[4] Because $H_2^+ + He$ is calculated to have highly structured resonance spectra,[19–22] the present energy resolution will have to be improved for a definitive test of theory. Resolution is limited by space-charge repulsion that occurs at the ion densities needed to obtain adequate signal. Operating closer to the neutral beam source, where the He density is much greater, should allow lower ion densities and proportionately better resolution ($\Delta E_c < 0.05$ eV). In addition the experiment will benefit from REMPI excitation schemes offering lower ionization efficiency but better H_2^+ (v,j) state selection.

The scattering/detection geometry used here is also

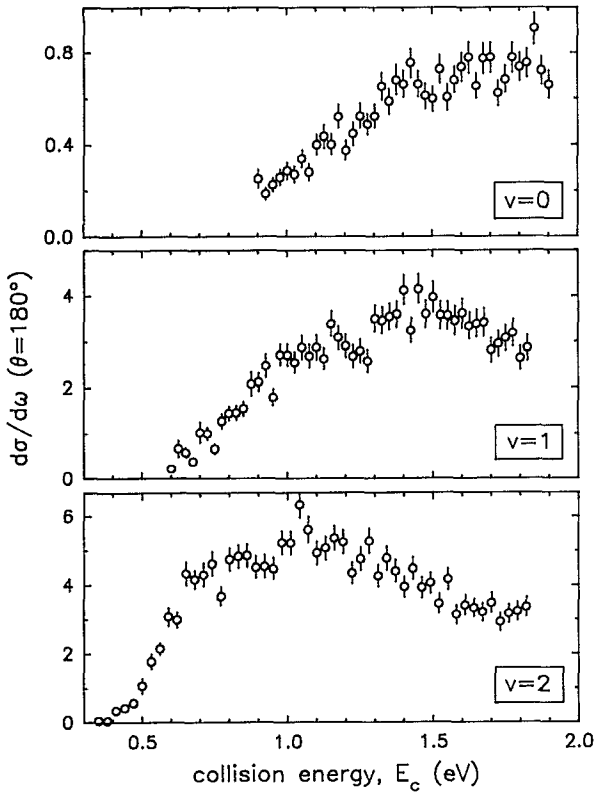

FIG. 3. Differential reaction cross section $d\sigma/d\omega(\theta = 180°)$ for H_2^+ $(v,j = 1)$ + He→HeH^+ + H. Error bars are derived from counting statistics (± one standard deviation). The relative units on the ordinate are consistent for all plots. The vibrational purity of H_2^+ (v) is given in the text.

applicable to *neutral* atom–diatom reactions. The H + H_2 reaction may be a favorable case because the predicted resonances[5] are broader and less dense than for H_2^+ + He. A complete state-to-state measurement is possible using methods previously reported (i.e., para-H_2 reacting with H atoms generated from HI photodissociation, followed by product quantum state analysis by REMPI[4,7,10]). The present method has the additional advantages of (1) preparing jet-cooled reactants for better ΔE_c resolution and (2) providing differential reaction cross sections at $\theta = 180°$ as a function of E_c. The H atom velocity vector, aligned by the laser polarization, has an angular distribution that is broad compared to the use of reactant ion acceleration, however, the effective breadth would be reduced because of the decreased collision probability away from the centerline of the molecular beam. Miller and coworkers recently suggested a prescription for detecting scattering resonances.[5] Their 3D calculations for H + H_2 show enhanced reactive scattering probabilities that appear as ridges in the (E_c, θ) plane.[25] This structure is specific to a particular product internal state and disappears when summed over j'. If our technique detects low-J reactive scattering with minimal averaging of j', then the E_c-dependent measure of $P_{v,j}$ represents a cut across the (E_c, θ) plane at $\theta = 180°$, and should therefore reveal resonance structure.

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[1] (a) A. Kuppermann, in *Potential Energy Surfaces and Dynamics Calculations*, edited by D. G. Truhlar (Plenum, New York, 1981), p. 375; (b) *Resonances*, edited by D. G. Truhlar (American Chemical Society, Washington D.C., 1984).
[2] R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford, New York, 1987), pp. 276ff and pp. 327ff.
[3] D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, and Y. T. Lee, J. Chem. Phys. **82**, 3045 (1985).
[4] J.-C. Nieh and J. J. Valentini, J. Chem. Phys. **92**, 1083 (1990).
[5] (a) W. H. Miller and J. Z. H. Zhang, J. Phys. Chem. **95**, 12 (1991); (b) R. E. Continetti, J. Z. H. Zhang, and W. H. Miller, J. Chem. Phys. **93**, 5356 (1990).
[6] (a) M. Zhao, D. G. Truhlar, N. C. Blais, D. W. Schwenke, and D. J. Khouri, J. Chem. Phys. **94**, 6696 (1990); (b) M. Zhao, D. G. Truhlar, D. W. Schwenke, and D. J. Khouri, *ibid.* **94**, 7074 (1990).
[7] D. A. V. Kliner, D. E. Adelman, and R. N. Zare, J. Chem. Phys. **94**, 1069 (1991).
[8] (a) S. A. Buntin, C. Giese, and W. R. Gentry, J. Chem. Phys. **87**, 1443 (1987); (b) Chem. Phys. Lett. **168**, 513 (1990).
[9] R. E. Continetti, B. A. Balko, and Y. T. Lee, J. Chem. Phys. **93**, 5719 (1990).
[10] D. L. Phillips, H. B. Levine, and J. J. Valentini, J. Chem. Phys. **90**, 1600 (1989).
[11] T. Turner, O. Dutuit, and Y. T. Lee, J. Chem. Phys. **81**, 3475 (1984).
[12] The total angular momentum J of an atom–diatom complex is designated as the vectorial sum of orbital and diatom rotational angular momenta, denoted by the quantum numbers l and j, respectively. The orbital angular momentum is a function of b and χ.
[13] T. Joseph and N. Sathyamurthy, J. Chem. Phys. **86**, 704 (1987).
[14] (a) N. C. Blais, R. B. Bernstein, and R. D. Levine, J. Phys. Chem. **89**, 10 (1985); (b) N. C. Blais and D. G. Truhlar, Chem. Phys. Lett. **102**, 120 (1983).
[15] J. E. Pollard, L. K. Johnson, and R. B. Cohen (unpublished).
[16] (a) J. E. Pollard, D. A. Lichtin, and R. B. Cohen, Chem. Phys. Lett. **152**, 171 (1988); (b) J. E. Pollard, L. K. Johnson, D. A. Lichtin, and R. B. Cohen (unpublished).
[17] M. A. O'Halloran, S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, J. Chem. Phys. **87**, 3288 (1987).
[18] R. Wolfgang and R. J. Cross, J. Phys. Chem. **73**, 743 (1969).
[19] J. D. Kress, R. B. Walker, and E. F. Hayes, J. Chem. Phys. **93**, 8085 (1990).
[20] J. Z. H. Zhang, D. L. Yeager, and W. H. Miller, Chem. Phys. Lett. **173**, 489 (1990).
[21] (a) D. J. Kouri and M. Baer, Chem. Phys. Lett. **24**, 37 (1974); (b) J. T. Adams, Chem. Phys. Lett. **33**, 275 (1975).
[22] N. Sathyamurthy, M. Baer, and T. Joseph, Chem. Phys. **114**, 73 (1987).
[23] (a) W. A. Chupka and M. E. Russell, J. Chem. Phys. Chem. **49**, 5426 (1968); (b) T. R. Govers and P.-M. Guyon, J. Chem. Phys. **113**, 425 (1987); (c) V. Pacák, U. Havemann, Z. Herman, F. Schneider, and L. Zülicke, Chem. Phys. Lett. **38**, 205 (1977).
[24] J. Tennyson and S. Miller, J. Chem. Phys. **87**, 6648 (1987).
[25] The notation $\sigma(\theta, E)$ used by Miller and Zhang (Ref. 5) for differential cross section corresponds to the quantity $d\sigma/d\omega$ measured here (except that E is total energy in Ref. 5).