Experimental determination of the specific opacity function for the Ba + HI \rightarrow Bal($\nu = 0$) + H reaction

Patrick H. Vaccaro,^{a)} Athanassios A. Tsekouras, Daqing Zhao,^{b)} Christine A. Leach,^{c)} and Richard N. Zare^{d)}

Department of Chemistry, Stanford University, Stanford, California 94305-5080

(Received 16 September 1991; accepted 5 November 1991)

Through the use of laser-induced fluorescence spectroscopy, product rotational population distributions were recorded for the Ba(${}^{1}S_{0}$) + HI($X {}^{1}\Sigma {}^{+}$) \rightarrow BaI($X {}^{2}\Sigma {}^{+}$, v = 0) + H(${}^{2}S_{1/2}$) reaction under well-defined, crossed-beam conditions. In this kinematically constrained reaction, orbital angular momentum of the reagents L_{reag} is channeled almost exclusively into rotational angular momentum of the products J_{prod} . Consequently, $|J_{prod}| \simeq \mu v_{rel} b$, where μ is the reduced mass of the reactants, v_{rel} is their relative velocity, and b is the impact parameter of the reactive collision. For relative velocity distributions with mean values ranging from 860 to 1000 m s $^{-1}$, the BaI v = 0 rotational distributions were found to peak sharply at high J values (≥ 420). Nonlinear least-squares analysis showed the specific opacity function (impact parameter distribution) for the formation of vibrationless BaI product to be exceptionally narrow ($\sim 0.3 \text{ Å FWHM}$) with a pronounced maximum at the highest energetically allowed impact parameter $\sim 4.5 \text{ Å}$.

I. INTRODUCTION

The modern science of molecular reaction dynamics is a multifaceted one, with the continuous development of experimental techniques intertwined with the ever more sophisticated nature of theoretical methodologies. At the most rudimentary level are studies that entail the measurement of macroscopic quantities, such as reaction rates and cross sections, fully averaged over all initial and final states as well as over all collision energies and geometries. More refined results are provided by differential angular distributions,¹ with complementary information derived from the specification of initial reagent state and the determination of final product-state distributions.² The most sophisticated and detailed knowledge of reactive processes is obtained from "doubly differential cross sections," in which the angular and state distributions of product molecules are measured simultaneously.³ Perhaps even more daunting is the task of observing directly the transition state;^{4,5} clearly such realtime studies, which are only crudely developed at present, point toward improved understanding of chemical transformations at their most fundamental level.

This paper reports on a recent series of measurements that strive for the same type of highly refined information as provided by doubly differential cross sections. Our experimental studies combine the high resolution of laser spectroscopy with the translational control afforded by molecular beam techniques to obtain an extraordinarily detailed picture of elementary gas-phase reaction dynamics. Through systematic examination of the reaction system

where all species are in their ground electronic states, we have determined the probability of reaction to form a specific product internal state as a function of the impact parameter b, defined as the distance of closest approach for a hypothetical undeflected trajectory of the colliding reagents.^{1,6} An average is normally performed over this fundamental dependence of reactivity on b in state-to-state measurements that do not include analysis of angular distributions. Elucidation of the subtle relationship between initial impact parameter and final product state provides an opportunity to explore, at a hitherto unprecedented level of sophistication, the influence that reagent stereospecificity (i.e., reagent approach geometry) exerts upon the dynamics of elementary bimolecular reactions.

Although the conceptual and theoretical foundations required to extract impact parameter information from isolated atom-diatom exchange reactions were recognized some time ago,⁷ only recently have technological developments made the experimental measurement of such quantities tractable. With laser-induced fluorescence (LIF) spectroscopy serving as a quantum-state-specific probe of BaI($X^{2}\Sigma^{+}$) product molecules, we have been able to exploit the kinematic (mass-dependent) constraint imposed on the Ba(${}^{1}S_{0}$) + HI($X^{1}\Sigma^{+}$) system to examine the detailed dependence of reactivity upon reagent approach geometry. Initial experiments, performed in our laboratory under beam-gas conditions,8 successfully measured the velocity- and orientation-averaged distribution of b values responsible for the formation of BaI in v = 8. Assuming that no energy barrier exists in the entrance channel of the reaction and that no explicit dependence of reactivity on velocity needs to be taken into account, Noda et al.8 found the impact parameter distribution to peak strongly at b = 2.6 Å with a

^{a)} Present address: Department of Chemistry, Yale University, New Haven, Connecticut 06511.

^{b)} Present address: Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, California 94305-5055.

^{e)} Née Montgomerie. Present address: Department of Chemistry, University of Southampton, Southampton, SO9 5NH, United Kingdom.

^{d)} Author to whom correspondence should be addressed.

narrow width of approximately 1.0 Å.

The limited range of impact parameters that contribute to the formation of BaI product in v = 8 can be attributed to kinematic and energy-balance requirements. A simple model, based on constant product recoil energy, was put forward to rationalize these observations.⁹ Nevertheless, the broad distribution of reagent translational energies produced by beam-gas experimental conditions, as well as the inability to vary this distribution significantly, severely restricted the interpretation of these early studies. In particular, no detailed information on the velocity dependence of the reagent impact parameter distribution could be obtained.

A more detailed understanding of the role that initial approach geometry plays in governing the outcome of a chemical transformation requires greater control over the relative collision energy of the reactants. Consequently, the present work exploited a crossed-beam experimental configuration, in which beams of Ba(${}^{1}S_{0}$) and HI($X^{1}\Sigma^{+}$) are made to interact under well-defined, single-collision conditions. By determining internal-state populations for the nascent BaI($X^{2}\Sigma^{+}$) molecules through the detailed analysis of high-resolution LIF spectra, we have been able to ascertain the distributions of reagent impact parameters responsible for the formation of individual product vibrational states.

The following section reviews the theoretical foundations that permit reagent impact parameter information to be deduced from the internal-state distributions of nascent product molecules. Here special emphasis is placed upon the validity and rigor of such arguments as applied to the present crossed-beam investigations. After a brief description of experimental techniques, we interpret the results derived from our spectroscopic measurements in terms of the energetic and kinematic constraints that govern the Ba + HI system. In particular, this work has enabled the detailed characterization of reagent impact parameters responsible for the formation of vibrationless BaI($X^{2}\Sigma^{+}$) product molecules. This information, when combined and contrasted with the data obtained from previous beam-gas studies, suggests a simple impulsive model for the scattering dynamics of the Ba + HI reaction.

II. THEORETICAL FOUNDATIONS

Contemporary studies of reaction dynamics ignore, for the most part, the detailed dependence of reaction cross section on both reagent impact parameter b and relative reagent orientation γ . Although orientation specificity has been demonstrated by selectively preparing reagent molecules using either external field interactions¹⁰⁻¹² or optical pumping schemes,¹³⁻¹⁵ control over the choice of impact parameter in a bimolecular collision is currently beyond the scope of experimental abilities. Consequently, the observed reaction cross section $\sigma(v_{rel})$ for some initial relative velocity, v_{rel} , can be expressed as an average over both b and γ , each weighted by an appropriate distribution function [viz., $2\pi b$ and $f(\gamma)$, respectively],

$$\sigma(v_{\rm rel}) = \int_b \int_{\gamma} P(b, v_{\rm rel}, \gamma) f(\gamma) d\gamma \, 2\pi b \, db, \qquad (2)$$

where $P(b, v_{rel}, \gamma)$, known as the total opacity function, de-

scribes the overall reaction probability for a given set of b, v_{rel} , and γ . It must be stressed that the averaging procedure embodied in this equation causes a loss of stereospecific information, which, in turn, hinders a microscopic interpretation for $\sigma(v_{rel})$.

As first suggested by Herschbach,⁷ the seemingly unavoidable averaging over b can be circumvented, under appropriate experimental conditions, so as to glimpse the detailed role that the reagent impact parameter plays in governing the outcome of a reactive encounter. Here a kinematically constrained reaction is chosen in which a heavy atom H collides with a heavy-light diatomic molecule H'L to produce a heavy-heavy diatomic molecule HH' and a light atom L,

$$H + H'L \rightarrow HH' + L.$$
(3)

Owing to the unique mass combination of such systems, the reagent orbital angular momentum L_{reag} is conserved almost exclusively as product rotational angular momentum J_{prod} ,

$$\mathbf{L}_{\text{reag}} \approx \mathbf{J}_{\text{prod}}.$$
 (4)

The magnitude of L_{reag} is related to b through the reduced mass μ and relative velocity v_{rel} of the reagents,

$$\mathbf{L}_{\text{reag}} \mid = \mu v_{\text{rel}} b. \tag{5}$$

Measurement of rotational distributions for the HH' diatomic product, at known v_{rel} , enables the relative impact parameter to be extracted. In particular, the *specific opacity* function $P_v(b,v_{rel},\gamma)$, which describes the reactive impact parameter distribution responsible for the formation of product molecules within a *single vibrational state v*, can be determined. The total opacity function appearing in Eq. (2) can be recast as a sum of $P_v(b,v_{rel},\gamma)$ over all final vibrational states of the product,

$$P(b,v_{\rm rel},\gamma) = \sum_{v} P_v(b,v_{\rm rel},\gamma).$$
(6)

The detailed shape of $P_v(b, v_{rel}, \gamma)$ thus provides a direct view of the intimate relationship between the initial approach geometry of the reactants and the final-state distribution of the products, as mediated by the potential energy surface or surfaces that govern a particular chemical reaction.

Although the complete determination of specific opacity functions is a fundamental, longstanding goal of our research efforts, experimental limitations usually require the definition of quantities more averaged than $P_v(b,v_{rel},\gamma)$. In particular, if no attempt is made to control the relative orientation of the reagents, an orientation-averaged specific opacity function, $P_v(b,v_{rel})$, must be considered,

$$P_{v}(b,v_{\rm rel}) = \int_{\gamma} P_{v}(b,v_{\rm rel},\gamma)f(\gamma)d\gamma.$$
⁽⁷⁾

Similarly, for experiments based upon a broad distribution of reagent collision energies, a velocity- and orientationaveraged specific opacity function $P_v(b)$ is most appropriate,

$$P_{v}(b) = \int_{v_{\rm rel}} \int_{\gamma} P_{v}(b, v_{\rm rel}, \gamma) f(\gamma) d\gamma f(v_{\rm rel}) dv_{\rm rel}, \qquad (8)$$

where $f(v_{rel})$ denotes the distribution of relative velocities for the reagents. Note that the v_{rel} dependence of the specific

2787

opacity function can be probed even in the absence of a truly monoenergetic distribution of relative reagent velocities. In particular, such information can be obtained by systematically varying $f(v_{rel})$ [cf. Eq. (8)] and observing the effect on $P_v(b)$.

The Ba(${}^{1}S_{0}$) + HI($X {}^{1}\Sigma {}^{+}$) reaction provides a prototypical example of the H + H'L atom-diatom exchange processes required for the extraction of specific opacity functions. The origin and rigor of the kinematic constraint imposed upon this system can be succinctly demonstrated through direct application of angular momentum conservation to the reagents and products of an isolated bimolecular collision,

$$\mathbf{L}_{\text{reag}} + \mathbf{J}_{\text{reag}} = \mathbf{L}_{\text{prod}} + \mathbf{J}_{\text{prod}}, \tag{9}$$

where J_{reag} and J_{prod} denote vectorial sums of angular momenta (e.g., rotational, electron-orbital, electron-spin, nuclear-spin, etc.) within the reagents and products, respectively. Whereas the values of J_{reag} and J_{prod} must be derived from a detailed spectroscopic analysis of internal-state distributions, the corresponding orbital angular momenta L_{reag} and L_{prod} follow from the translational dynamics of the reactive scattering event [cf. Eq. (5)].

For the Ba(${}^{1}S_{0}$) + HI($X {}^{1}\Sigma^{+}$) system, \mathbf{J}_{reag} can be expressed formally as the vectorial sum of J_{Ba} and J_{HI} . The ¹S₀ electronic state of the atomic barium reagent immediately suggests that $J_{Ba} = 0.16$ The HI utilized for the present studies was prepared via a well-defined supersonic expansion that produced a beam of reactant molecules in their $X^{1}\Sigma^{+}$ ground state. Because this electronic manifold has no intrinsic spin or orbital angular momentum,¹⁷ only rotational motion can contribute to J_{HI} . Although not directly determined, the effective temperatures for vibrational and rotational degrees of freedom in our $HI(X^{1}\Sigma^{+})$ source must be somewhere between the stagnation temperature for the supersonic nozzle (\sim 323 K) and the experimentally measured translational temperature for the beam (≤ 20 K); values closer to the lower bound are much more probable. For both of these limiting cases, the large vibrational constant ($\omega_e = 2309.01 \text{ cm}^{-1}$)¹⁸ requires essentially all molecules to be in their lowest vibrational state. The rotational and centrifugal distortion constants for the v = 0 level of $(B_e = 6.4264 \text{ cm}^{-1}, D_e = 2.069)$ $HI(X^{1}\Sigma^{+})$ $\times 10^{-4}$ cm⁻¹)¹⁸ yield average rotation angular momenta of approximately 5 h at 323 K and 0.75 h at 20 K. When compared with the magnitudes and uncertainties ascribed to other quantities involved in the kinematic constraint, J_{HI} can be set approximately equal to zero such that

$$\mathbf{J}_{\text{reag}} = \mathbf{J}_{\text{Ba}} + \mathbf{J}_{\text{HI}} \approx 0. \tag{10}$$

In a similar manner, the internal angular momentum of the products \mathbf{J}_{prod} can be expressed as the vectorial sum of \mathbf{J}_{H} and \mathbf{J}_{BaI} . The departing hydrogen atom is formed in its ${}^{2}S_{1/2}$ ground electronic state, where $|\mathbf{J}_{\text{H}}| = \frac{1}{2} \hbar$. For the BaI $(X^{2}\Sigma^{+})$ product, the angular momentum derived from electron spin (viz., $|\mathbf{S}| = \frac{1}{2}\hbar$) couples with that arising from the end-over-end motion of the nuclear framework, to yield half-integral values for the rotational quantum numbers.¹⁹ The small rotational constants that characterize the groundstate potential surface of this heavy-heavy diatomic species²⁰ suggest that even moderate partitioning of available energy into product rotation will translate into a significant amount of stored angular momentum. Since J_{BaI} can readily approach several hundred \hbar in magnitude, it is quite reasonable to assume that

$$\mathbf{J}_{\text{prod}} = \mathbf{J}_{\text{H}} + \mathbf{J}_{\text{BaI}} \approx \mathbf{J}_{\text{BaI}},\tag{11}$$

where the value of J_{BaI} must be determined from detailed analysis of the rotational state populations in the nascent BaI product molecules.

The partitioning of angular momentum within translational degrees of freedom can be deduced from the definitions of $|\mathbf{L}_{reag}|$ and $|\mathbf{L}_{prod}|$ as provided by Eq. (5). For the Ba + HI system, the vastly different values for the reduced masses of the reactants and the products (viz., $\mu_{Ba-HI} = 66.36$ amu and $\mu_{BaI-H} = 1.004$ amu) imply a considerable difference between the magnitudes of the corresponding orbital angular momenta. This characteristic feature forms the basis of the kinematic constraint and is readily confirmed through simple model calculations. Assuming a maximum reagent impact parameter of ~ 5 Å, which yields a very reasonable hard-sphere reactive cross section of approximately 80 Å² (Ref. 21), the average relative velocity attained during the present crossed-beam study [e.g., \overline{v}_{rel} (Ba-HI) = 900 m s⁻¹] suggests that $|\mathbf{L}_{reag}| = 470 \hbar$. This crude estimate for the angular momentum of the reactants [cf. Eqs. (9) and (10)] is quite comparable to that observed in the rotational state distributions of the nascent BaI product molecules.

A similar calculation for the orbital angular momentum of the products is complicated by the lack of any detailed experimental information on either the final recoil energy or the departing impact parameter. Although the magnitude of v_{rel} (BaI-H) is expected to be small,²² the hypothetical situation obtained when all available energy is channeled directly into translational motion of the products is interesting to consider. By combining the recently determined reaction exorgicity of $\Delta E = 7.3 \pm 2.0$ kcal mol⁻¹ (Ref. 23) with our measured average translational energy for the reactants [viz., \overline{E}_{rel} (Ba-HI) = 7.54 kcal mol⁻¹], this limiting case yields a maximum possible recoil velocity $v_{\rm rel}$ (BaI-H) = 1.1×10⁴ m s⁻¹. Substituting this quantity into an expression analogous to that of Eq. (5) and assuming that the final impact parameter is comparable to the H-I bond distance [i.e., r_e (HI) = 1.604 Å],¹⁸ it is readily shown that $|\mathbf{L}_{prod}| \approx 25 \, \hbar$. This minute result and the fact that theoretical^{9,22} and experimental^{21,23} studies point to only slight partitioning of available energy into product translation lead to the justifiable approximation that

$$|\mathbf{L}_{\text{prod}}|\approx 0. \tag{12}$$

The above discussion of angular momentum partitioning has served to elucidate the microscopic origins of the kinematic constraint imposed upon the Ba + HI system. In particular, the fundamental relationship employed for our extraction of specific opacity function information from reactive scattering data can be readily derived from the conservation law of Eq. (9),

 $|\mathbf{L}_{\text{reag}}| = \mu_{\text{Ba-HI}} v_{\text{rel}} (\text{Ba-HI}) b \approx |\mathbf{J}_{\text{prod}}| \approx |\mathbf{J}_{\text{BaI}}|.$ (13)Further corroboration of Eq. (13) can be found in the semiclassical trajectory studies performed by Siegel and Schultz²⁴ on the analogous, albeit less constrained, $Ba + HCl \rightarrow BaCl + H$ reaction. This work revealed an exceptionally strong linear correlation between $|L_{reag}|$ and $|\mathbf{J}_{prod}|$ that was only slightly influenced by details of the potential energy surface used to model the chemical transformation. Trajectory calculations conducted in our laboratory on the Ba + HI system have also pointed to a neardirect channeling of L_{reag} into J_{prod}.²⁵ Similar results follow from the analytical scattering dynamics of a crude collinear approximation to the Ba + HI hypersurface.²⁶ Here massweighted cluster coordinates²⁷ yield a skew angle of 86.33°, which suggests essentially complete transformation of reagent orbital angular momentum into rotational motion of the diatomic product.1

A rigorous application of angular momentum conservation principles would require the kinematic constraint to be formulated in terms of total internal angular momentum **F**, rather than only the "rotational" angular momentum **J**. Here, by definition, **F** is given by the vectorial sum of **J** and the nuclear spin angular momentum **I**. The experimental uncertainties ascribed to the various quantities involved in the present study, however, argue against this additional level of complexity. Therefore, the ensuing analysis is based exclusively on the angular momentum **J** with nuclear spin degrees of freedom justifiably neglected. This procedure is tantamount to assuming that nuclear spin acts as a "spectator" in the Ba + HI reaction system.²⁸

III. EXPERIMENT

The apparatus and techniques used in our investigation of the Ba + HI reaction system are described elsewhere.²³ Only a summary of the most relevant experimental details is presented here.

All experiments were performed in a crossed-beam reaction chamber designed to permit the intersection of "effusive" barium and supersonic hydrogen iodide beams at a 90° geometry. Extensive use of differential pumping ensured that high-vacuum ($\sim 10^{-7}$ Torr), single-collision conditions were maintained in the interaction region. A slightly supersonic beam of $Ba({}^{1}S_{0})$ was produced by collimating the output of a radiatively heated crucible (~1350 K) containing barium metal. The HI($X^{1}\Sigma^{+}$) reagent was prepared via a skimmed and collimated supersonic expansion in various carrier gases. Changes in the nature of the carrier gas (i.e., He, N₂, or Ar) and/or the concentration of HI (typically $\leq 6\%$) enabled the relative collision energy in the center-of-mass frame to be varied from roughly 0.2 to 0.5 eV. Reagent velocity distributions were measured directly by means of high-resolution, two-photon Doppler spectroscopy for $Ba({}^{1}S_{0})$ and through quadrupole-based time-of-flight mass spectrometry for HI($X^{1}\Sigma^{+}$).

Rotational and vibrational state distributions for the nascent BaI product were deduced from high-resolution LIF spectra excited and monitored through the BaI $C^2\Pi - X^2\Sigma^+$ transition at ~550 nm. The excitation source

for our LIF detection scheme was provided by a singlemode, cw ring dye laser, which had an actively stabilized linewidth of <1 MHz. Use of an integral wave meter in conjunction with computer-controlled frequency scanning and data acquisition enabled high-resolution, continuousstream spectra to be recorded over the entire tuning range available to a given dye. The dye laser output was actively power stabilized, spatially filtered, and collimated before being propagated through the Ba + HI interaction region in a direction orthogonal to the plane defined by the crossed reagent beams. Lock-in detection, based on modulation of the probe laser, enabled us to discriminate the resulting LIF signal from residual background noise.

IV. RESULTS

A. Rotational state distributions of Bal(v=0)

As suggested by Eq. (13), the extraction of specific opacity functions from reactive scattering data requires knowledge of the rotational state distributions for individual product vibrational levels. Consequently, the populated internal states of our nascent BaI ($X^{2}\Sigma^{+}$) molecules must be identified and labeled with a definitive set of vibrational and rotational quantum numbers. The detailed spectroscopic information demanded for such an analysis proves to be the major technical stumbling block for direct implementation of the kinematic constraint as originally proposed by Herschbach more than 20 years ago.7 In particular, despite the efforts of numerous research groups, 29,30 the BaI $C^{2}\Pi - X^{2}\Sigma^{+}$ system utilized for the present LIF measurements still lacks a complete and unambiguous rovibronic assignment. The specific difficulties associated with the spectroscopy of BaI have been described elsewhere²³ and are mentioned only briefly.

Figure 1 depicts a detailed Fortrat diagram for the BaI $C^2\Pi_{1/2} - X^2\Sigma^+$ (0,0) band as derived from work performed in our laboratory.^{29,31} A similar set of Fortrat parabolas is obtained for analogous rovibronic transitions to the other spin-orbit excited state $C^2\Pi_{3/2}$, which is located ~756 cm⁻¹ above the $C^2\Pi_{1/2}$ state. Although the large mass of the heavy-heavy BaI product is required for rigorous appli-



FIG. 1. Fortrat diagram for the BaI $C^2 \Pi_{1/2} - X^2 \Sigma^+$ (0,0) subband. The almost identical (1,1) diagram is situated approximately 6 cm⁻¹ to the blue, whereas the (0,0) Fortrat diagram for the other spin-orbit subband is located roughly 756 cm⁻¹ to the blue.

cation of the kinematic constraint, it also makes analysis of the nascent rotational distributions a quite formidable task. In part, this difficulty stems from the small, nearly equal rotational constants for the C and X states ($B \approx 0.027$ cm^{-1}),²⁹ which, in conjunction with the presence of six distinct rotational branches per spin-orbit manifold, lead to the formation of exceptionally congested vibronic bands. The nonbonding nature of the electron involved in the C-X transition³² requires the upper state potential surface to be essentially identical, in shape and position, to that of the ground state. Consequently, Franck-Condon factors strongly favor $\Delta v = 0$ vibronic bands that are separated in frequency by only the relatively small difference in vibrational constants between the C and the X states (viz., $\omega_e^{II} - \omega_e^{\Sigma} \simeq 6 \text{ cm}^{-1}$).³³ As a consequence, a closely spaced sequence of (v,v) Fortrat parabolas arises such that the resulting density of rovibronic transitions requires the use of techniques normally reserved for hyperfine analysis just to resolve rotational fine structure.34,35

Previous beam-gas studies of the Ba + HI reaction^{8,36} were able to isolate individual rovibronic transitions within the BaI $C^{2}\Pi - X^{2}\Sigma^{+}$ (8,8) vibronic band by making use of selectively detected laser-induced fluorescence (SDLIF) spectroscopy. Unfortunately, the substantial loss in overall signal intensity that accompanies the monochromator-based implementation of this technique precluded its use under the more rarefied conditions afforded by our crossed-beam experimental configuration. As a result, the present beambeam measurements are based on a somewhat different strategy, which focuses on the relatively well-isolated $P_2(J)$ and $P_{12}(J)$ branches for the lowest $\Delta v = 0$ vibronic transitions in the Bal C-X system (cf. Fig. 1). In particular, this scheme has permitted us to characterize the distribution of reagent impact parameters responsible for the formation of BaI product molecules in their vibrationless ground state.

Figure 2 demonstrates how fully resolved rovibronic LIF spectra, yielding unambiguous BaI($X^{2}\Sigma^{+}$) rotational distributions, have been obtained through a judicious choice of experimental conditions. Here the uppermost panel depicts the high-resolution LIF spectrum observed by scanning the frequency of our probe laser through the entire BaI $C^{2}\Pi_{1/2} - X^{2}\Sigma^{+} \Delta v = 0$ band system while simultaneously monitoring the undispersed fluorescence signal emitted by the nascent BaI product molecules. These data, taken from the crossed-beam reaction of a "thermal" Ba(${}^{1}S_{0}$) source with a supersonic expansion of 6% HI($X^{1}\Sigma^{+}$) in a carrier gas mixture of N2 and He, correspond to an average relative translational energy of 7.60 kcal mol⁻¹ with a one-standarddeviation spread of 1.47 kcal mol⁻¹. This distribution of reagent translational energy, combined with the excergicity of the Ba + HI system (i.e., $\Delta E = 7.3 \pm 2.0 \text{ kcal mol}^{-1}$) as derived from our recent measurement of $D_0^0(BaI)$,²³ suggests that product vibrational states up to $v \approx 37$ should be energetically accessible under the present experimental conditions.

While the actual experimental data depicted in the uppermost panel of Fig. 2 might appear somewhat noisy, closer inspection reveals this "noise" to be primarily a consequence of individual rovibronic transitions resolved by our single-



FIG. 2. BaI $C^{2}\Pi_{1/2} - X^{2}\Sigma^{+} \Delta v = 0$ spectrum obtained under crossed-beam conditions. The upper panel shows the complete (v,v) sequence. The middle panel (a detail of the red end of the upper panel) shows only P_{12} branch members of the (0,0), (1,1), and (2,2) bands and the $(0,0)P_{1}$ bandhead (offscale). The lower panel (a detail of the low wave number section of the middle panel) shows only $(0,0)P_{12}$ branch members. The $(0,0)P_{12}$ bandhead to $(1,1)P_{12}$ bandhead at 17 780.8 cm⁻¹.

mode excitation laser. A detailed analysis of the vibronic features exhibited by the long-range BaI LIF spectrum is reported elsewhere,²³ and a more systematic study of their dependence upon initial reagent translational energy is in progress. Of particular importance, however, is that the lowest $\Delta v = 0$ vibronic bands clearly display the sharp doublet features associated with the formation of blue-shaded $P_1(J)$ and $Q_{12}(J)$ bandheads. In contrast, the higher (v,v) vibronic bands exhibit only a regular modulation of spectral intensity with no pronounced features. This oscillatory pattern can be attributed to dense regions of rovibronic structure that result from low rotational excitation (viz., J < 350) of individual vibrational levels in the nascent BaI product.

For the investigation of specific opacity functions, the rotational distributions exhibited by individual vibrational levels of the nascent product are of primary concern. The central panel of Fig. 2 shows a detailed view of the low-frequency region from the long-range BaI LIF spectrum. Although the P_1 (J) and Q_{12} (J) "double" bandheads for the lowest $\Delta v = 0$ vibronic bands are evident, insufficient prod-

uct rotational excitation exists under the present crossedbeam experimental conditions for the creation of "high-J" $P_{12}(J)$ bandhead features [i.e., $E_{\rm rot}$ (BaI) < 0.9 eV]. Nevertheless, clusters of spectral lines, corresponding to $P_{12}(J)$ branch members with J values less than those required for bandhead formation, can be readily identified.

The lowermost portion of Fig. 2 displays an extremely magnified view of the BaI $C^2 \Pi_{1/2} - X^2 \Sigma^+$ LIF spectrum in a region corresponding to the $P_{12}(J)$ branch of the (0,0) vibronic band. This panel clearly illustrates how fully resolved $P_{12}(J)$ rovibronic transitions totally free of overlapping vibronic congestion can be obtained under HI/N₂/He beambeam conditions. In view of the near-identical transition probabilities for the high-J lines of the $P_{12}(J)$ branch,³⁷ the overall shape of the rotational distribution associated with the vibrationless BaI product can be ascertained readily from the figure.

The upper portion of Fig. 3 displays a high-resolution, 1.6 cm⁻¹ segment of the BaI LIF spectrum recorded under HI/N₂ crossed-beam conditions. The individual members of the $P_{12}(J)$ branch, which is analogous to the $P_2(J)$ branch of the $C^2\Pi_{3/2} - X^2\Sigma^+$ system, are cleanly resolved, and each has been assigned a definitive value of the rotational quantum number J. Single rovibronic transitions exhibit an average linewidth of approximately 600 MHz with



FIG. 3. BaI $C^2 \Pi_{1/2} - X^2 \Sigma^+$ (0,0) P_{12} branch members. In the upper panel each line is labeled by J''. In the lower panel the hyperfine structure of the first two lines that appear in the upper panel is partly resolved and each component is labeled by F'' and J''. Note the appearance caused by the $\Delta F = \Delta J$ propensity rule.

detailed shapes that can be attributed to hyperfine structure. The lower panel of Fig. 3 depicts two rotational lines of the $P_{12}(J)$ branch under Doppler-limited resolution. Here the hyperfine features that arise from the coupling of the iodine nuclear spin (I = 5/2) to the rotational angular momentum of BaI are clearly revealed.¹⁷ Spectroscopic transitions, resulting from the predominant selection rule $\Delta F = \Delta J$, have been labeled through extrapolation of BaI hyperfine measurements recently performed in our laboratory.³⁸

Both Figs. 2 and 3 show a quasicontinuous background, which we attribute to the weak $\Delta v = -1$ sequence in the region of v = 25. In extracting relative intensities, a constant offset was subtracted from the height of each rotational line. This offset was determined at the low wavenumber end of the spectrum (see Fig. 2, lower panel), where only unresolved features are present.

Figure 4 shows a measured distribution of rotational population in vibrationless $BaI(X^2\Sigma^+)$ formed under $HI/N_2/He$ crossed-beam conditions. The v = 0 rotational distribution, as derived for the F_2 spin-rotation components via the $P_{12}(J)$ or $P_2(J)$ rovibronic transitions, peaks strongly at $J \sim 420$ and exhibits an exceptionally narrow width of approximately 60 \hbar . The completely non-Boltzmann nature of this result reflects the selective population of individual angular momentum states as dictated by the influence of the kinematic constraint. The average rotational excitation of the vibrationless product is $\overline{E}_{rot}(v=0) \approx 0.6$ eV, which is roughly isoenergetic with the rotationless level of BaI in v = 34!

B. Reagent velocity distributions

To invert rotational populations into specific opacity functions, we need to know a precise value for the relative velocity of the reactants. Figure 5 depicts the velocity distributions independently measured for our effusive Ba and supersonic HI/N₂/He sources. Under these experimental conditions, which correspond to those employed for extraction of the BaI(v = 0) population data in Fig. 4, translational temperatures of 731 \pm 2 K and 10.2 \pm 0.1 K are determined



FIG. 4. BaI (v = 0) product rotational population distributions. Both data sets were recorded during the same experimental run. One distribution (circles) was measured via the BaI $C^2\Pi_{1/2} - X^2\Sigma^+$ (0,0) P_{12} branch (cf. Fig. 2, lower panel) and the other (crosses) via the $C^2\Pi_{3/2} - X^2\Sigma^+$ (0,0) P_2 branch.

Downloaded 08 Aug 2002 to 18.85.3.141. Redistribution subject searcary regard, see http://ojps.aip.org/jcpc/jcpcr.jsp



FIG. 5. Beam velocity distributions. The experimentally determined distribution parameters (and their 1σ uncertainties) for the experiment marked with an asterisk in Table I are $v_0 = 247.6(3) \text{ m s}^{-1}$, $v_s = 234.6(1) \text{ m s}^{-1}$, and $\alpha_s = 296.9(4) \text{ m s}^{-1}$ for the Ba beam and $v_s = 758.9(2) \text{ m s}^{-1}$ and $\alpha_s = 36.5(1) \text{ m s}^{-1}$ for the HI beam. The expected thermal Ba velocity distribution for a Ba beam at the same temperature (1310 K) is also shown (dotted line). Velocity parameters follow the definitions of Ref. 23.

for the Ba and HI reagents, respectively. The slightly supersonic nature of the Ba(${}^{1}S_{0}$) beam is clearly demonstrated by the dotted curve in Fig. 5, which denotes the velocity profile expected for a Maxwell–Boltzmann (i.e., thermal) distribution of barium atoms having an effective temperature set equal to that of the oven crucible (viz., ~1310 K).

Figure 6 illustrates the distribution of reagent relative velocities v_{rel} (Ba–HI) associated with the same experimental conditions. This plot was derived from the independently measured velocity profiles for the Ba(${}^{1}S_{0}$) and HI(X ${}^{1}\Sigma$ $^{+}$) reagent beams by converting them to the center-of-mass coordinate frame and numerically convoluting them together subject to the constraints imposed by the 90° crossing geometry of our reaction apparatus.³⁹ The mean, most probable, and standard deviation for the calculated relative velocity



FIG. 6. Relative velocity distribution for the experiment marked with an asterisk in Table I. The measured distribution peaks at 921 m s⁻¹ and has a mean value of 961 m s⁻¹ and a standard deviation of 89 m s⁻¹. The relative velocity distribution for a beam-gas experiment (Ref. 8) (dotted line) peaks at 600 m s⁻¹ and has a mean value of 638 m s⁻¹ and a standard deviation of 241 m s⁻¹.

distribution are given in the figure caption.

The dotted curve in Fig. 6 represents the relative velocity profile reported in a recent beam-gas investigation of the Ba + HI reaction system.⁸ The spread in our crossed-beam $v_{\rm rel}$ (Ba-HI) distribution is more than a factor of 4 narrower than that of the previous beam-gas study. In view of the kinematic constraint, this decrease in the width of the relative velocity profile should facilitate the deconvolution of quantitative reagent impact parameter information from observed product rotational state distributions.

C. Summary of experiments

The present analysis of specific opacity functions for the Ba + HI system is based on a collection of nine data sets, the parameters of which have been summarized in Table I. Each of these experiments entailed the concurrent measurement of rotational population distributions for the vibrationless BaI($X^{2}\Sigma^{+}$) product and beam velocity distributions for both the Ba(${}^{1}S_{0}$) and HI($X {}^{1}\Sigma^{+}$) reagents. The studies reported here span relative collision energies whose average values range from 0.23 to 0.37 eV. Crossed-beam conditions that yield a mean collision energy outside of these limits do not permit complete isolation of the BaI(v=0) rotational distribution, as illustrated in Fig. 2. In particular, higher translational energies, obtained by increasing the stream velocity from the HI supersonic source, lead to the formation of bandheads in the P_2 and P_{12} branches that hamper the extraction of detailed population data for individual rovibronic levels. On the other hand, lower translation energies gave rise to a significant degradation in the quality of observed BaI LIF spectra, most probably as a result of the decrease in product concentration that accompanies reduction in the velocity of the HI reagent.

V. ANALYSIS

Our goal is to find a model for the specific opacity function that simulates the observed distribution of rotational population for the BaI(v = 0) product. Although several functional forms for $P_0(b,v_{rel})$ have been tried,⁴⁰ the ensuing discussion will focus on four examples, of varying complexity, that reveal interesting features of the Ba + HI system.

The population n(J) of BaI(v = 0) product characterized by the rotational quantum number J is given by the expression

$$n(J) = \int_0^\infty \int_0^\infty 2\pi b v_{\rm rel} P_0(b, v_{\rm rel}) \\ \times f(v_{\rm rel}) \delta(J - J') db \, dv_{\rm rel}, \qquad (14)$$

where $P_0(b, v_{rel})$ is the specific opacity function whose form is to be determined, $f(v_{rel})$ is the experimental relative velocity distribution, and the Dirac delta function expresses the kinematic constraint imposed upon the magnitude of J, namely,

$$|\mathbf{J}'| = \hbar [J'(J'+1)]^{1/2} = \mu v_{\rm rel} b,$$
(15)

where we have replaced \mathbf{J}_{prod} by \mathbf{J}' .

Previous beam-gas measurements on the Ba + HI system have demonstrated that only a narrow range of reagent

TABLE I. Measured parameters for crossed-beam experiments in which the BaI(v = 0) rotational distribution was probed. The data are presented in order of ascending values of the mean relative velocity. Velocity parameters follow the definitions of Ref. 23. The asterisk denotes the experimental results that are used as examples in Secs. IV and V and in Figs. 2 (middle and lower panels), 4, 5, 6, 7, and 9.

	Ba beam		HI beam		Relative velocity		Rotational distributions			
Label*	vo	<i>v</i> _s	α,	v _s	α,	Vmean	FWHM	$J_{\rm mp}^{\ b}$	J _{mean}	FWHM
а	227	268	295	646	31.9	875	234	405.5	401	52
b	253	177	323	694	30.9	915	229	410.5	404	59
	253	177	323	694	30.9	915	229	414.5	404	59
с	183	242	306	721	30.1	919	227	410.5	405	62
d	259	311	282	736	35.7	959	217	415.5	417	59
c*	248	235	297	759	36.5	961	210	418.5	414	63
*	248	235	297	759	36.5	961	210	421.5	413	59
	251	392	252	741	32.9	965	208	426.5	420	55
f	251	392	252	741	32.9	965	208	425.5	420	58
g	183	281	296	785	31.1	976	217	428.5	418	58
ĥ	276	451	224	770	30.8	996	191	429.5	427	61
i	234	267	292	849	34.9	1035	200	427.5	422	57

* Labeled rotational distributions are shown in Fig. 8.

^bRotational state with largest population.

impact parameters, spread over roughly 1 Å, contributes to the formation of BaI (v = 8).⁸ These studies also concluded that analysis of the v = 8 reactive scattering data did not require the incorporation of an explicit velocity dependence into the specific opacity function. However, when applied to the present BaI (v = 0) results, such velocity-independent modeling procedures consistently predicted rotational distributions that were substantially broader than those observed experimentally. This behavior follows from the predominant role that the broad spread of relative reagent velocities plays in governing the overall population of rotational states in the BaI product [cf. Eq. (15)].

Interpretation of our BaI(v=0) reactive scattering data requires the simultaneous consideration of both angular momentum and energy conservation. In contrast to BaI(v = 8), the BaI(v = 0) product is subject to an energybased cutoff, above which insufficient energy exists for the formation of product molecules in high-J rotational states. The spread in total energy available for the Ba + HI reaction, which arises from the initial distribution of translational energy in the reagents, implies that this upper bound on J will be velocity dependent. Consequently, the specific opacity function for BaI(v = 0) should contain an explicit dependence on v_{rel} that derives from the requirements of energy conservation. Equation (15) uniquely maps each (b, v_{rel}) pair into a particular product J state that, in turn, is restricted to be lower in energy than some velocity-dependent cutoff. Consequently, $P_0(b, v_{rel})$ will exhibit a velocitydependent maximum value of the impact parameter $b_{\rm max}(v_{\rm rel})$ beyond which reaction can no longer occur. Indeed, energy constraints were found to truncate all of the model opacity functions utilized for the simulation of our BaI(v=0) results.

The product state restrictions imposed by energy conservation readily follow from the partitioning of available energy between internal and translational degrees of freedom. Briefly, for BaI(v = 0),

$$E_{\rm rel} + \Delta E = E_{\rm rot} + E_{\rm rec}, \qquad (16)$$

where

$$E_{\rm rel} = \frac{1}{2}\mu_{\rm Ba-HI}v_{\rm rel}^2 \tag{17}$$

is the relative collision energy of the reactants with reduced mass μ_{Ba-HI} , ΔE is the reaction excergicity defined by²³

$$\Delta E = D_0^0 (BaI) - D_0^0 (HI),$$
 (18)

 $E_{\rm rot}$ is the rotational energy of the BaI(v = 0) product,³¹ and

$$E_{\rm rec} = \frac{1}{2}\mu_{\rm BaI-H}v_{\rm rec}^2 \tag{19}$$

is the recoil energy of the products with reduced mass $\mu_{\text{BaI-H}}$.

In the absence of any detailed information on the recoil energy of the products, the conservation criterion of Eq. (16) places a velocity-dependent upper bound on the amount of energy that can be deposited into rotational motion for the BaI(v = 0) product,

$$E_{\rm rot} \leq E_{\rm rel} + \Delta E.$$
 (20)

This cutoff in rotational energy translates into a velocitydependent upper limit, $J_{max}(v_{rel})$, for the range of rotational quantum numbers that can be populated in the BaI(v = 0)product. Subsequently, application of the kinematic constraint yields the maximum value that the reactive impact parameter can attain for a given relative velocity,

$$b_{\max}(v_{\rm rel}) = \frac{\hbar}{\mu_{\rm Ba-HI}v_{\rm rel}} \times \{J_{\max}(v_{\rm rel}) [J_{\max}(v_{\rm rel}) + 1]\}^{1/2}.$$
 (21)

It is evident that application of energy conservation to the Ba + HI system requires detailed knowledge of the reaction excergicity ΔE as defined by Eq. (18). Although the dissociation energy for HI is believed to be known with high accuracy [viz., D_0° (HI) = 70.429 \pm 0.025 kcal mol⁻¹],¹⁸ the corresponding quantity for BaI has long been a matter of considerable contention and speculation. Based upon the application of energy-balance arguments to the reactants and products of crossed-beam reactions, we have recently reported a lower limit for D_0^0 (BaI) of 76.8 \pm 1.7 kcal mol⁻¹ (Ref. 23). When combined with the upper bound of D_0^0 (BaI) = 78.5 \pm 0.5 kcal mol⁻¹ derived from earlier predissociation studies,⁴¹ our measurements suggest a BaI bond energy of 77.7 \pm 2.0 kcal mol⁻¹. This value, yielding an exoergicity of $\Delta E = 7.3 \pm 2.0$ kcal mol⁻¹ for the Ba + HI \rightarrow BaI + H system, is in good agreement with the mass spectrometric results recently obtained by Hildenbrand.⁴²

A simple but misleading form for $P_0(b, v_{rel})$ can be drawn from the ubiquitous hard-sphere model for reactive encounters.¹ Here the overall probability for reaction is usually expressed in terms of a total opacity function [cf. Eq. (2)] that is equal to unity for all impact parameters less than some maximum value b_{max} and zero otherwise. Although this predicted behavior might appear to be overly simplistic, trajectory calculations performed on the kinematically constrained Ba + HCl/HBr systems have verified a steplike functionality for $P(b, v_{rel})$ and have rationalized its occurrence through a centrifugal or angular momentum barrier.²⁴ These studies also demonstrated the hard-sphere shape for the total opacity function to be relatively independent of reagent collision energy and potential energy hypersurface. In contrast, the magnitude of b_{max} was found to depend quite strongly on both of these dynamical quantities.

A plausible hard-sphere model for the BaI(v = 0) specific opacity function might have the form

$$P_{0}(b, v_{\rm rel}) = H[b_{\rm max}(v_{\rm rel}) - b], \qquad (22)$$

where $b_{\max}(v_{rel})$ is defined by Eq. (21) and $H[b_{\max}(v_{rel}) - b]$ denotes a Heavyside function that is equal to unity for $b \le b_{\max}(v_{rel})$ and zero otherwise. Note that an explicit velocity dependence has been incorporated into $P_0(b, v_{rel})$ through consideration of the restrictions imposed upon b_{\max} by virtue of energy-balance requirements.

To test the validity of a hard-sphere model for the BaI(v = 0) specific opacity function, a nonlinear leastsquares regression was performed simultaneously on the nine data sets compiled in Table I. Here the relative velocity distributions determined for the reagents were convoluted, in the manner suggested by the kinematic constraint, with a steplike distribution of impact parameters as described by Eq. (22). Because separate experimental measurements of v = 0 rotational populations are not absolutely calibrated in amplitude, each data set was assigned an independent scaling factor that was determined within the nonlinear fit. For this analysis, the only adjustable quantity of dynamical significance was the BaI dissociation energy D_0^0 (BaI), which served to define the velocity-dependent cutoff for reactive impact parameters.

Figure 7(a) depicts the results of modeling the specific opacity function for BaI(v = 0) by the hard-sphere form of Eq. (22). Clearly, the simulated rotational distribution generated by this procedure is much too broad, with significant population predicted to exist in low angular momentum states. Furthermore, as shown in Table II, the BaI bond dissociation energy derived from this analysis is greater than the upper bound of 78.5 \pm 0.5 kcal mol⁻¹ imposed by ear-



FIG. 7. Experimental and simulated rotational population distributions with their associated model opacity functions. All panels show data for the experiment marked with an asterisk in Table I. In each panel a different form for $P_0(b,v_{rel})$ is used, as described in the text. The opacity functions are drawn for $v_{rel} = 921$ m s⁻¹, which is the most probable relative velocity for this experiment. Optimized parameter values are given in Table II.

lier predissociation studies.⁴¹ Therefore, we conclude that all impact parameters consistent with the energy conservation criterion of Eq. (20) cannot lead to reaction with equal probability.

Noda and Zare⁹ have suggested a particularly simple theory for explaining the dynamical consequences of kinematically constrained reactions. Here the relative recoil energy in the products is assumed to be constant, so that

$$f(E_{\rm rec}) = \delta(E_{\rm rec} - E_0), \qquad (23)$$

where E_0 is a positive number. Taking into account the energy-balance requirements of Eq. (16), this "constant product recoil" (CPR) model implies that the specific opacity function responsible for the formation of BaI(v = 0) product should be of the form

$$P_{\rm o}(b, v_{\rm rel}) = \frac{A}{2\pi b_{\rm o}(v_{\rm rel})v_{\rm rel}} \delta[b - b_{\rm o}(v_{\rm rel})], \qquad (24)$$

where A is a proportionality constant that depends on the experimental conditions and $b_0(v_{rel})$ is obtained by solving Eq. (16) for the impact parameter subject to the condition that $E_{rec} = E_0$. This calculation of $b_0(v_{rel})$ is analogous to that utilized for the determination of $b_{max}(v_{rel})$ except that the value of ΔE utilized for Eq. (21) must be replaced by $\Delta E - E_0$. Note once again that energy conservation has led

TABLE II. Parameter values for model opacity functions as derived from nonlinear least-squares analyses performed on the rotational distribution marked with an asterisk in Table I.

Label*	Model	χ^2	Parameter (1 σ uncertainty)
a	Step function	42.9	$D_0^0(\text{BaI}) = 79.20(24) \text{ kcal mol}^{-1}$
b	Constant product recoil	18.8	D_0^0 (BaI) $-E_{\rm rec} = 76.66(4)$ kcal mol ⁻¹
с	Fixed truncated Gaussian	1.79	$b_0 = 6.09(5)$ Å, $\sigma_b = 0.85$ Å ^b D_0^0 (BaI) = 78.42(2) kcal mol ⁻¹
d	Sliding truncated Gaussian	1.36	$\lambda = -2.11(8), \sigma_b = 0.85 \text{ Å}^{b}$ $D_0^{0}(\text{BaI}) = 77.88(3) \text{ kcal mol}^{-1}$

* Labels used in Fig. 7 for the same model.

^bFixed.

to the incorporation of an explicit velocity dependence into the v = 0 specific opacity function.

The validity of the CPR model was assessed by performing a global least-squares regression on the experimental data sets compiled in Table I. For this analysis, the only adjustable parameter of dynamical significance could be equated with the quantity $D_0^0(BaI) - E_0$. A value of 76.64 \pm 0.02 kcal mol⁻¹ was obtained for $D_0^0(BaI) - E_0$, which, given the recently determined BaI bond energy of 77.7 \pm 2.0 kcal mol⁻¹ (Ref. 23), is in good agreement with the expected small magnitude of $E_{\rm rec}$ (viz., E_0) in the Ba + HI system.⁹

Comparison of the experimental and calculated v = 0 rotational distributions, as illustrated in Fig. 7(b), reveals qualitative agreement. From this we conclude that the specific opacity function must be strongly peaked as a function of b. More detailed examination of Fig. 7(b) shows that the CPR model fits well the high-J part of the distribution but fails on the low-J part.

Comparison of the results generated from the hardsphere and CPR simulations suggests that a more satisfactory form for the v = 0 specific opacity function should allow reactivity to peak near $b_{max}(v_{rel})$ while still retaining a finite range of reactive impact parameters that extends toward smaller *b* values. Two schemes that fulfill these criteria have been examined. In one, known as the "fixed truncated Gaussian" model, $P_0(b,v_{rel})$ is given by

$$P_{\rm o}(b, v_{\rm rel}) = \exp\left[-\frac{1}{2}\left(\frac{b-b_0}{\sigma_b}\right)^2\right] H\left[b_{\rm max}(v_{\rm rel})-b\right],$$
(25)

where the adjustable parameters are b_0 , the center of the Gaussian, σ_b , proportional to the width of the Gaussian, and D_0^0 (BaI), which is used in the calculation of the velocity-dependent maximum value of the impact parameter $b_{max}(v_{rel})$ [cf. Eq. (21)].

The parameter values determined from a global nonlinear least-squares regression of our data sets with the fixed truncated Gaussian model for $P_0(b, v_{rel})$ are contained in the caption to Fig. 8. Figure 7(c) shows a comparison of the observed and calculated rotational distributions for BaI(v = 0) in the specific test case we have chosen. Clearly, the agreement between theory and experiment is quite satisfactory, although the range of reagent relative velocities is limited in the present studies. In addition, the BaI bond dissociation energy derived from this analysis is consistent with that obtained from previous energy-balance measurements.²³

In another scheme for the v = 0 specific opacity function, an attempt was made to retain a near-constant reaction probability over the full range of relative reagent velocities. For this "sliding truncated Gaussian" model, the form of $P_0(b,v_{rel})$ was taken to be the same as that given in Eq. (25) but b_0 was assumed to be a function of v_{rel} ,

$$b_0 = b_{\max}(v_{\rm rel}) - \lambda \sigma_b, \tag{26}$$

where λ is an adjustable scaling factor.

The numerical results generated from the sliding truncated Gaussian model are contained in Table II and a com-



FIG. 8. Experimental and simulated rotational distributions. The experimental distributions (circles) are labeled as in Table I. The solid lines are best-fit simulations derived from a global nonlinear least-squares fit to the nine data sets with different relative velocities using the sliding truncated Gaussian model. The parameters calculated (and their 1 σ uncertainties) were $\lambda = -2.01(5)$, $\sigma_b = 0.85$ (fixed) Å, and D_0° (BaI) = 77.95(2) kcal mol⁻¹. The corresponding results for the fixed truncated Gaussian model are $b_0 = 5.14(9)$ Å, $\sigma_b = 0.59(3)$ Å, and D_0° (BaI) = 78.48(1) kcal mol⁻¹.

parison of the predicted v = 0 rotational distribution with that determined from experimental measurements is shown in Fig. 7(d). As in the case of the fixed truncated Gaussian scheme, a quite satisfactory agreement is found between the calculated and observed product-state populations. This point is reinforced by Fig. 8, which displays the velocitydependent simulations obtained from the sliding truncated Gaussian opacity function for each of the data sets included in the present study. As might be expected, the BaI dissociation energy derived from this analysis is also in good accord with the currently accepted value of D_0^0 (BaI).^{23,42}

Despite their inherent differences, both of the truncated Gaussian models for the v = 0 specific opacity function provide equally good simulations of our experimental results. This stems primarily from the limited range of reagent relative velocities probed in the present study. Furthermore, the severe truncation of reactive impact parameters introduced by the restrictions of energy conservation yields nearly identical shapes of P_0 (b, v_{rel}) for the fixed and sliding Gaussian forms over the range of v_{rel} investigated.

The conclusions deduced from our opacity function analyses can best be understood by reference to the truncated Gaussian model results presented in Fig. 9. Here we show a contour map of the BaI(v = 0) doubly differential cross section, which is defined, in analogy of Eq. (2), by

$$\frac{\partial^2 \sigma_0}{\partial b \, \partial v_{\rm rel}} = 2\pi b P_0 \left(b, v_{\rm rel} \right) f(v_{\rm rel}). \tag{27}$$

The coordinate axes for this plot are provided by the independent reaction variables of b and v_{rel} with dotted lines superimposed so as to denote reactive encounters that involve specific amounts of angular momentum. The dashed curve serves to divide the (b,v_{rel}) plane into energetically accessible and inaccessible regions, as suggested by the quantity b_{max} (v_{rel}) defined in Eq. (21). Although the CPR model for $P_0(b,v_{rel})$ would predict reactivity to be concentrated

only along the dash-dot line, the truncated Gaussian form clearly provides for a range of reactive impact parameters at any given relative reagent velocity. More importantly, for the experimental conditions utilized in the present study [viz., $f(v_{rel})$], only a narrow distribution of impact parameters is found to lead to the formation of BaI molecules in v = 0. All other b values do not contribute to the formation of BaI(v = 0), i.e., they give rise to BaI in other vibrational states or they lead to no reaction.

VI. CONCLUSIONS

The BaI (v = 0) product formed from the crossed-beam reaction of Ba + HI \rightarrow BaI + H is found to be highly rotationally excited. The rotational quantum-state distribution peaks near J = 420 and exhibits an exceptionally narrow width of approximately 60 Å. Careful selection of experimental conditions, designed to avoid the extensive overlap of vibronic structure inherent to the optical spectroscopy of BaI, enabled product rotational populations to be obtained for several different relative reagent velocities. Although the peak of the v = 0 rotational distribution shifts to higher J values with increasing v_{rel} , its overall shape does not appear to change significantly (see Fig. 8).

By using conservation of energy and angular momentum, we could determine the approximate form of the specific opacity function leading to formation of BaI(v = 0). This opacity function peaks close to the energy-limited impact parameter (~4.5 Å), is very narrow (FWHM $\simeq 0.3$ Å), and is extremely asymmetric. Since the experimental data do not cover a wide range of relative velocities and are subject to signal-to-noise limitations, their analysis could not determine the detailed shape of the opacity function. In any event, the reactive impact parameters deduced from our study are much larger than the classical outer turning point (i.e., ~3.2 Å) of vibrational motion for BaI(v = 0) molecules excited to high-lying rotational levels. This strongly suggests that



J. Chem. Phys., Vol. 96, No. 4, 15 February 1992

Downloaded 08 Aug 2002 to 18.85.3.141. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

the Ba–I bond distance decreases prior to ejection of the H atom and formation of the BaI(v = 0) product.

The maximum impact parameter decreases slowly as a function of relative reagent velocity in a manner determined by the reaction exoergicity. This dependence enabled the nonlinear least-squares analyses performed for the determination of specific opacity functions to derive a new estimate for the dissociation energy of BaI, viz., $D_0^0(BaI) = 78.2 \pm 0.5$ kcal mol⁻¹. This value is comparable with our previously reported value of 77.7 ± 2.0 kcal mol⁻¹ (Ref. 23).

Energy conservation imposes an upper bound of roughly 1.1×10^4 m s⁻¹ for the relative recoil velocity of the BaI and H products. However, the model opacity functions deduced from the present study suggest a somewhat lower value of $v_{\rm rec} \approx 3.5 \times 10^3$ m s⁻¹. Based on a "worst-case" estimate for the departing impact parameter [viz., sum of the HI bond length and half of the BaI(v = 0) bond length, where the latter is taken at the outer turning point], this recoil velocity corresponds to a maximum product orbital angular momentum of only 18 Å. Therefore, $|\mathbf{J}_{\rm prod}| \ge |\mathbf{L}_{\rm prod}|$, and the key approximation of the kinematic constraint, that $|\mathbf{L}_{\rm reag}| \approx |\mathbf{J}_{\rm prod}|$, is well satisfied for the Ba + HI reaction system.

When compared and contrasted with the results derived from earlier beam-gas studies.⁸ the reactive scattering data of the present study reveals several interesting trends. Both the v = 0 and v = 8 specific opacity functions are exceptionally narrow and well localized in the (b, v_{rel}) plane (see Fig. 9). Moreover, the average or most probable impact parameter moves toward lower values with increasing product vibrational excitation. This behavior, which has been corroborated by ongoing beam-gas work in our laboratory, suggests a simple, impulsive model for the Ba + HI system. Here, through detailed consideration of the classical mechanics for colliding particles, reactive encounters involving small impact parameters should yield vibrationally excited product molecules that are in turn rotationally cold. Conversely, large impact parameter collisions give rise to product molecules in low vibrational states, with substantial excitation in rotational degrees of freedom. Thus the decomposition of $P(b, v_{rel})$ into the sum of $P_v(b, v_{rel})$ resembles the shell structure of an onion [see Eq. (6)].

Taken to its logical extension, the simple impulsive model may be used to estimate the total cross section for the Ba + HI reaction and to provide a qualitative explanation for the form of the vibrational population distribution. The BaI(v = 0) product arises from the largest reactive impact parameter, whereas the BaI($v = v_{max}$) product arises from $b \simeq 0$. Therefore, assuming $b_{max} = 4.5$ Å leads to a hardsphere total cross section of $\pi b_{max}^2 = 64$ Å². This value is in good agreement with that suggested by earlier work.²¹ Because energy conservation truncated those larger values of b that contribute lower vibrational levels, and because the population in a vibrational level increases as the square of the impact parameter, these two effects work together to yield a bell-shaped population distribution of the vibrational levels. Such distributions have been observed under beam-gas conditions.^{8,21} Similar arguments might also explain this characteristic behavior exhibited by the Ba + HX reaction family, where X = F, Cl, Br, and I.²¹ Measurements designed to explore the specific opacity function for Ba + HI as a function of the vibrational level of the BaI product are currently in progress.

ACKNOWLEDGMENTS

The authors thank C. Noda for useful discussions. P. H. V. thanks the IBM Corporation for support through a postdoctoral research fellowship. C. A. L. thanks the SERC for a NATO postdoctoral fellowship. This work was supported by the National Science Foundation under Grant Nos. NSF CHE 85-05926 and NSF CHE 89-21198.

- ¹R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University, New York, 1987).
- ² D. J. Rakestraw, K. G. McKendrick, and R. N. Zare, J. Chem. Phys. 87, 7341 (1987); R. Zhang, D. J. Rakestraw, K. G. McKendrick, and R. N. Zare, *ibid.* 89, 6283 (1988); R. Zhang, W. J. van der Zande, M. J. Bronikowski, and R. N. Zare, *ibid.* 94, 2704 (1991).
- ³ D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, and Y. T. Lee, J. Chem. Phys. 82, 3045 (1985); D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobatake, R. K. Sparks, T. P. Schafer, and Y. T. Lee, *ibid.* 82, 3067 (1985).
- ⁴ R. B. Bernstein and A. H. Zewail, J. Chem. Phys. **90**, 829 (1989); M. Dantus, M. J. Rosker, and A. H. Zewail, *ibid.* **89**, 6128 (1988); A. H. Zewail, Science **242**, 1645 (1988); M. J. Rosker, M. Dantus, and A. H. Zewail, *ibid.* **241**, 1200 (1988); M. Dantus, M. J. Rosker, and A. H. Zewail, J. Chem. Phys. **87**, 2395 (1987).
- ⁵ P. R. Brooks, Chem. Rev. 88, 407 (1988); T. C. Maguire, P. R. Brooks, R. F. Curl, J. H. Spence, and S. J. Ulvick, J. Chem. Phys. 85, 844 (1986); T. C. Maguire, P. R. Brooks, and R. F. Curl, Phys. Rev. Lett. 50, 1918 (1983).
- ⁶I. W. M. Smith, *Kinetics and Dynamics of Elementary Gas Phase Reactions* (Butterworths, London, 1980).
- ⁷D. R. Herschbach, Faraday Discuss. Chem. Soc. 33, 281 (1962); D. R. Herschbach, Adv. Chem. Phys. 10, 319 (1966).
- ⁸C. Noda, J. S. McKillop, M. A. Johnson, J. R. Waldeck, and R. N. Zare, J. Chem. Phys. **85**, 856 (1986).
- ⁹C. Noda and R. N. Zare, J. Chem. Phys. 86, 3968 (1987).
- ¹⁰ P. R. Brooks, Science **193**, 11 (1976); G. Marcelin and P. R. Brooks, J. Am. Chem. Soc. **95**, 7885 (1973); E. M. Jones and P. R. Brooks, J. Chem. Phys. **53**, 55 (1970); P. R. Brooks, E. M. Jones, and K. Smith, *ibid.* **51**, 3073 (1969).
- ¹¹ S. R. Gandhi, Q.-X. Xu, T. J. Curtiss, and R. B. Bernstein, J. Phys. Chem. 91, 5437 (1987); S. R. Gandhi, T. J. Curtiss, Q.-X. Xu, S. E. Choi, and R. B. Bernstein, Chem. Phys. Lett. 132, 6 (1986); K. K. Chakravorty, D. H. Parker, and R. B. Bernstein, Chem. Phys. 68, 1 (1982).
- ¹² B. Friedrich and D. R. Herschbach, Nature (London) 353, 412 (1991).
- ¹³ R. N. Zare, Ber. Bunsenges. Phys. Chem. 86, 422 (1982).
- ¹⁴ M. Hoffmeister, R. Schleysing, and H. Loesch, J. Phys. Chem. **91**, 5441 (1987).
- ¹⁵C. T. Rettner and R. N. Zare, J. Chem. Phys. 77, 2416 (1982); 75, 3636 (1981).
- ¹⁶The most prevalent isotope of barium, ¹³⁸Ba, has an intrinsic nuclear spin angular momentum of zero [I(¹³⁸Ba) = 0]. The BaI molecules observed in the present study are believed to originate exclusively from the reactive scattering of this isotope with HI. Justification for this presumption can be found both in the 71.66% natural abundance of ¹³⁸Ba and in the detailed analysis of hyperfine structure for the nascent BaI($X^2\Sigma^+$) product.
- ¹⁷The single naturally occurring isotope of iodine, ¹²⁷I, has an intrinsic nuclear spin of 5/2 [I(¹²⁷I) = 5/2], which manifests itself as hyperfine splittings on individual rovibronic transitions of iodine-containing molecules. While such hyperfine interactions can be observed readily in the nascent BaI product and are presumed to exist in the HI reactant, the small magnitude of I(¹²⁷I) suggests that it can be neglected for the present kinematic analysis.
- ¹⁸ K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).
- ¹⁹G. Herzberg, Molecular Spectra and Molecular Structure. I. Spectra of

Diatomic Molecules (Van Nostrand Reinhold, New York, 1950).

- ²⁰ T. Törring and K. Döbl, Chem. Phys. Lett. 115, 328 (1985).
- ²¹ H. W. Cruse, P. J. Dagdigian, and R. N. Zare, Faraday Discuss. Chem. Soc. 55, 277 (1973); C. A. Mims, S.-M. Lin, and R. R. Herm, J. Chem. Phys. 57, 3099 (1972).
- ²² The potential energy hypersurface for the Ba + HI reaction system is expected to exhibit an early barrier that channels most of the exoergicity into product internal excitation rather than product recoil. See, for example, M. H. Mok and J. C. Polanyi, J. Chem. Phys. **51**, 1451 (1969).
- ²³ P. H. Vaccaro, D. Zhao, A. A. Tsekouras, C. A. Leach, W. E. Ernst, and R. N. Zare, J. Chem. Phys. 93, 8544 (1990).
- ²⁴ A. Siegel and A. Schultz, J. Chem. Phys. 76, 4513 (1982).
- ²⁵ D. Zhao and R. N. Zare (unpublished results).
- ²⁶ N. H. Hijazi and K. J. Laider, J. Chem. Phys. 58, 349 (1973).
- ²⁷ J. O. Hirschfelder, Int. J. Quantum Chem. 3, 17 (1969).
- ²⁸ J. Vigué, P. Grangier, and A. Aspect, Phys. Rev. A **30**, 3317 (1984); H. K. Haugen, E. Weitz, and S. R. Leone, J. Chem. Phys. **83**, 3402 (1985).
- ²⁹ M. A. Johnson, C. Noda, J. S. McKillop, and R. N. Zare, Can. J. Phys. 62, 1467 (1984).
- ³⁰ M. M. Patel and N. R. Shah, Indian J. Pure Appl. Phys. 8, 681 (1970); P. Mesnage, Ann. Phys. (Paris) 12, 5 (1939).
- ³¹ D. Zhao, P. H. Vaccaro, A. A. Tsekouras, C. A. Leach, and R. N. Zare, J.

Mol. Spectrosc. 148, 226 (1991).

- ³² P. J. Dagdigian, H. W. Cruse, and R. N. Zare, J. Chem. Phys. 60, 2330 (1974).
- ³³ M. L. P. Rao, D. V. K. Rao, P. T. Rao, and P. S. Murty, Fizika 9, 25 (1977).
- ³⁴ M. A. Johnson and R. N. Zare, J. Chem. Phys. 82, 4449 (1985).
- ³⁵ M. A. Johnson, C. R. Webster, and R. N. Zare, J. Chem. Phys. 75, 5575 (1981).
- ³⁶ C. A. Leach, J. R. Waldeck, C. Noda, J. S. McKillop, and R. N. Zare, J. Mol. Spectrosc. 146, 465 (1991).
- ³⁷ R. N. Zare, Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics (Wiley, New York, 1988).
- ³⁸ W. E. Ernst, J. Kändler, C. Noda, J. S. McKillop, and R. N. Zare, J. Chem. Phys. 85, 3735 (1986); C. A. Leach, W. E. Ernst, J. Kändler, C. Noda, J. S. McKillop, and R. N. Zare *ibid*. 95, 9433 (1991).
- ³⁹S. Datz, D. R. Herschbach, and E. H. Taylor, J. Chem. Phys. 35, 1549 (1961).
- ⁴⁰C. A. Leach, A. A. Tsekouras, P. H. Vaccaro, R. N. Zare, and D. Zhao, Faraday Discuss. Chem. Soc. **91** (in press).
- ⁴¹ M. A. Johnson, J. Allison, and R. N. Zare, J. Chem. Phys. 85, 5723 (1986).
- ⁴² D. L. Hildenbrand and K. H. Lau, J. Chem. Phys. (in press).