

that both rotational and vibrational wavefunctions of the molecule instantly adjust to the incoming atom while in the calculation of Wolken and Karplus only the coupling between rotational states are taken into account.

The most disturbing thing is the large difference between the differential cross sections of the present calculation and the close-coupling calculation. In Fig. 2, we plot  $\sigma(\theta) \sin\theta$  as a function of angle. The  $\sigma(\theta)$  used for close-coupling calculation is curve (b) of Fig. 1, which is what Wolken and Karplus used themselves for comparison of various results (see Fig. 10 of Ref. 2). The areas under the curves are then the total cross sections. It is seen that there are large contributions from  $0^\circ$  to  $90^\circ$  in the close-coupling calculation while in the adiabatic distorted wave calculation almost no contribution is from that region. Because of this difference, we must view the agreement between the total cross sections with caution. Further investigation on this

question will certainly be very useful.

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†Present address: Theoretical Chemistry Institute, University of Wisconsin, Madison, WI 53706.

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## Primitive angular distribution studies of internal states in crossed-beam reactions using laser fluorescence detection\*

Paul J. Dagdigan<sup>†</sup> and Richard N. Zare

Department of Chemistry, Columbia University, New York, New York 10027  
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Laser-induced fluorescence has recently been shown to be a sensitive detector capable of determining the internal state populations of products formed in gas-phase chemical reactions under single-collision conditions.<sup>1</sup> In previous experiments, however, the reaction zone and the laser excitation zone have coincided so that the detected signal is large. The present experiment demonstrates that the laser fluorescence detector has sufficient sensitivity to permit angular distribution studies to be performed on the individual internal states.

In order to maximize the product signal at a given angle, we have purposely chosen to study the reaction  $\text{Ba} + \text{LiCl} \rightarrow \text{BaCl} + \text{Li}$ , in which the  $\text{BaCl}$  product is kinematically constrained (see inset in Fig. 1) to lie close to the centroid (center-of-mass velocity vector). Figure 1 presents the excitation spectrum of  $\text{BaCl}$  taken at several laboratory scattering angles. Two ovens are mounted on a rotating flange and are operated under approximately effusive conditions. The  $\text{Ba}$  beam has an angular width of  $5^\circ$  FWHM, and the source slit is maintained at  $1230^\circ\text{K}$  (corrected pyrometer reading); the  $\text{LiCl}$  beam has a width of  $14^\circ$  FWHM, and the slit is at  $1180^\circ\text{K}$ . Although the  $\text{LiCl}$  slit is about  $80^\circ\text{K}$  hotter than the charge, the salt beam is estimated to contain  $\sim 20\%$  dimers.<sup>2</sup> Fortunately the reaction of  $\text{Ba}$  with  $(\text{LiCl})_2$  is expected to be  $35\text{ kcal/mole}$  endothermic,<sup>2,3</sup> so that the presence of  $(\text{LiCl})_2$  can be disregarded.

The reaction zone, defined as the intersection of the two beams, is on the axis of the rotating flange. The laser beam ( $0.2\text{ cm}$  diam) is in the scattering plane,<sup>4</sup> and the excitation zone is separated from the reaction

zone ( $22\text{ cm}$  away) by a collimating slit. In this manner, the laser detector subtends an angle of  $\sim 3^\circ$  about the reaction zone. The fluorescence excitation and detection equipment is similar to that employed previously. A

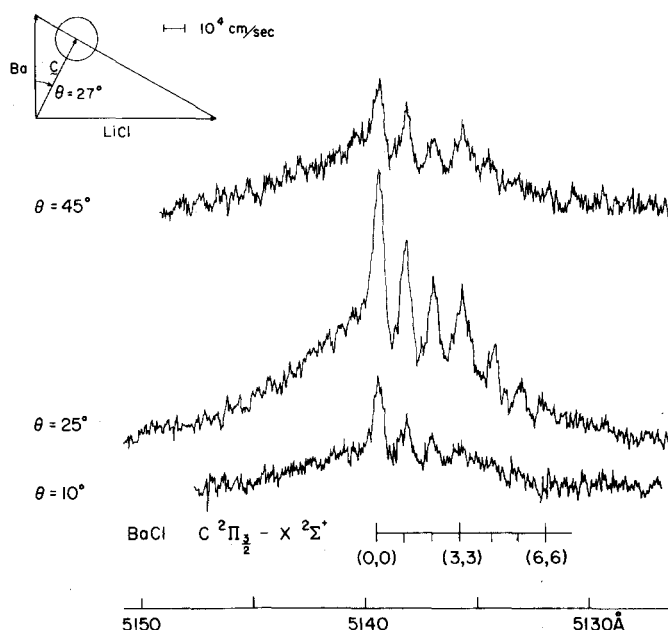


FIG. 1.  $\text{BaCl}$  excitation spectra taken at several laboratory angles  $\theta$ , measured from the  $\text{Ba}$  beam. The  $(v', v'')$  band heads of the  $\text{BaCl}$   $\text{C}-\text{X}$  system are marked. The inset shows a Newton diagram for the most probable velocities of the beams. The circle represents the locus of  $\text{BaCl}$  ( $v=0, J=0$ ) center-of-mass velocities, and  $\text{C}$  denotes the centroid vector.

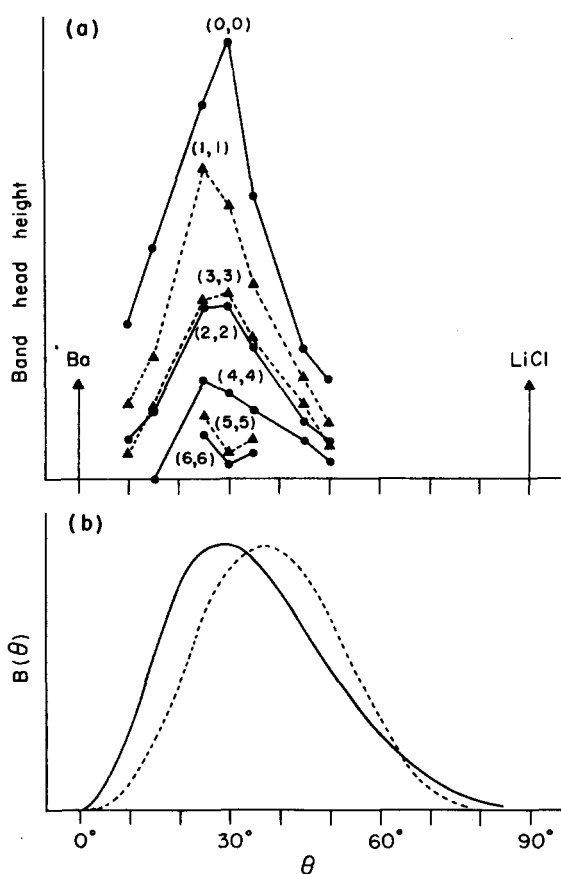


FIG. 2. (a) Laboratory angular distributions of the various BaCl vibrational states. (b) Centroid angular distributions  $B(\theta)$  for Maxwell-Boltzmann (solid line) and nonthermal (dashed line) beams, assuming an energy independent cross section. The nonthermal beam velocity distributions were derived from those measured by S.-M. Lin, C. A. Mims, and R. R. Herm [J. Chem. Phys. 77, 569 (1973)] for Ba, and by W. B. Miller, S. A. Safron, and D. R. Herschbach [J. Chem. Phys. 56, 3581 (1972)] for the alkali halide, using appropriate mass and temperature corrections.

Molelectron pulsed (15 pulse per sec) dye laser, with CSA-22 dye<sup>5</sup> (bandwidth 0.25 Å), is employed. Because of the weakness of the signal, full laser power is used. A PAR model 162 boxcar integrator with a 164 plug-in amplifies and averages the photomultiplier (RCA 7265) output with typically a 1 sec time constant. Spectra are obtained by sweeping the laser wavelength at  $\sim 1$  Å/min.

In Fig. 2(a) we have plotted as a function of laboratory scattering angle the heights of each band head above the "background" due to the other bands. The angular distributions of the various vibrational levels of BaCl are very similar to each other to within the  $\pm 10\%$  experimental uncertainties. Figure 2(b) illustrates several calculated centroid angular distributions.<sup>6</sup> At present we cannot say whether the products are scattered preferentially forward or backward in the center-of-mass

system.

The Ba + LiCl reaction is nearly thermoneutral. The vibrational distribution of the BaCl products, obtained by integrating the in-plane signal,<sup>7</sup> follows closely a Boltzmann distribution with a temperature approximately that of the ovens. From the observation that the  $v=6$  level is populated, we set a lower bound to the BaCl dissociation energy  $D_0^0(\text{BaCl}) \geq 110 \pm 3$  kcal/mole, based on the known value of  $D_0^0(\text{LiCl})^8$ . This may be compared with the lower bound (110 kcal/mole) obtained previously by Jonah and Zare<sup>8</sup> from the chemiluminescent reaction  $\text{Ba} + \text{Cl}_2$ . The actual value of  $D_0^0(\text{BaCl})$  is not likely to be significantly greater because (1) the BaCl vibrational distribution appears to be thermal, and (2) the angular distribution does not differ appreciably from the centroid distribution (see Fig. 2). Thus, the lower bound (119.7  $\pm 1.5$  kcal/mole) obtained by Menzinger and Wren<sup>9</sup> appears to be ruled out unless the BaCl is scattered predominantly sideways in the center-of-mass system.

We estimate that at the peak of the angular distribution approximately  $10^5$  molecules/cm<sup>3</sup> of BaCl in the  $v=0$  level are present in the excitation zone. With more sophisticated techniques than those employed here, we may anticipate that correspondingly lower densities of products can be detected and kinematically less constrained reactions can be studied.

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<sup>†</sup>Present address: Department of Chemistry, the Johns Hopkins University, Baltimore, MD 21218.

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