In a first approximation, we use the following approach to analyze the experimental data. Assuming the two-fraction fast-exchange model is valid, one can relate the observed relaxation rate \( (T_1)^{-1} \) to the reciprocal of the pore radius by the following expression:

\[
(T_1)^{-1} = (T_1)_{\text{bulk}}^{-1} + 2a/R \left[ (T_1)_S^{-1} - (T_1)_{\text{bulk}}^{-1} \right],
\]

where \((T_1)_{\text{bulk}}^{-1}\) is the relaxation rate for bulk liquid nitrobenzene-\(d_6\), \(T_1S\) is the relaxation time for the liquid in the surface layer, \(a\) is the thickness of the surface layer, and \(R\) is the pore radius. The linear relationship between \(1/T_1\) and \(1/R\) as shown in Fig. 1 implies the validity of the two-state model.\(^{2,12}\) By assuming that \(a\) is equal to twice the molecular diameter, one can estimate the average reorientational correlation time \(\tau_0 = 90\) ps for nitrobenzene-\(d_6\) in the surface layer. In contrast, for bulk nitrobenzene \(\tau_0 = 8.5\) ps. One may conclude that close to the surface the viscosity of nitrobenzene is about \(10\times\) greater than in the bulk liquid. Our value \(\tau_0 = 8.5\) ps obtained for bulk nitrobenzene agrees with our earlier measurements\(^{14}\) for nitrobenzene-\(d_5\) and with the value given by Warnock et al.\(^{1}\)

The freezing point depression of nitrobenzene in the porous glass was estimated from the disappearance of the NMR signal following a single-pulse experiment under high resolution conditions. The highest temperature at which bulk nitrobenzene gives no NMR signal is denoted as \(T_p\). The temperature at which the NMR signal disappears in the porous glass is denoted as \(T_M\). A linear relationship between \(T = T_p - T_M\) and \(1/R\) was found for our samples in agreement with the results obtained by Ritter et al.\(^3\) for alcohol in porous glasses.

Systematic NMR studies of fluids in pores using molecular liquids of different size, polarity and hydrogen-bonding ability are in progress together with differential scanning calorimetry measurements of the confinement effect on the glass transition in glass forming liquids.

We express our thanks to Dr. Peter G. Wolynes for bringing this problem to our attention. This work was partially supported by the National Science Foundation under Grant Nos. NSF DMR 86-12860 and NSF CHE 85-09870.

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**Time dependent three-dimensional body frame quantal wave packet treatment of the H+H₂ exchange reaction on the Liu–Siegbahn–Truhlar–Horowitz (LSTH) surface**

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(Received 3 January 1989; accepted 3 March 1989)

Recently, there has been much progress in the field of quantum mechanical reactive scattering theory.\(^{1-9}\) It is now possible to carry out fully converged, three-dimensional (3D) quantum mechanical calculations for hydrogen containing atom-diatomic systems. All of the published 3D reactive methods have been based on the time independent Schrödinger equation (or related equations for auxiliary functions such as the amplitude density)\(^{10}\). There has also
been significant progress made in the development of efficient, numerically exact methods for solving the time dependent Schrödinger equation by the propagation of wave packets.11-19 To date, however, 3D numerically exact wave packet studies have been restricted to nonreactive inelastic atom–diatom collisions15 and to molecule-corrugated surface collisions.13

In this paper we report the first successful application of the 3D quantum body frame wave packet approach to reactive scattering; specifically the approach is applied to the H + H2 exchange reaction on the LSTH potential surface.20 The method employed is based on a procedure for calculating total reaction probabilities (summed over all product states) from wave packets presented earlier by Neuhauser and Baer and applied successfully to the collinear H + H2 reaction.19 In the generalized version for 3D reactions, the propagation is done entirely using standard Jacobi coordinates for the initial arrangement, and a nonreactive, body frame wave packet propagation algorithm is employed. In order to treat reaction, the grid for the wave packet extends partway into the reactive arrangement channels. At each time step, we calculate the projection of the wave packet onto the reactive rovibrational eigenfunctions at a plane placed across the reactive arrangement channel, perpendicular to the reactive translational coordinate. From these projections, we can calculate the state resolved flux through that plane. The state-resolved reaction probabilities are then found by integrating through time the flux into the various open channel product states. If the flux plane is placed far enough out in the reactive channel, fully converged vibrationally and rotationally resolved reaction probabilities can be calculated. However, if one only desires probabilities which are vibrationally resolved but summed over rotational states, it is possible to move the plane much closer to the interaction region. This results in a substantial reduction in grid size. For H + H2, we found that converged vibrationally resolved reactive probabilities (but summed over rotational states) can be calculated with a grid not much larger than is needed for performing the pure inelastic calculation. To prevent the reactive portion of the wave packet from re-entering the strong interaction region after reflecting from the edge of the grid, we follow Neuhauser and Baer18,19 and employ an absorbing complex potential near the edge of the grid (see also Ref. 14).

In Table I, we give our results for several energies. All calculations were performed with total angular momentum J = 0 and with initial state ν = 0, j = 0. Above the first reactive vibrational threshold, energy resolved probabilities were obtained by employing broad spatial wave packets which were correspondingly narrow in momentum space and hence in total energy. Each energy therefore required a separate propagation. Below this threshold, we propagated a single narrow spatial wave packet and calculated the energy and state resolved inelastic probabilities over a wide range of energies.15 The reactive probabilities were then found by demanding that probability be conserved. We compare our results with those of Zhang et al.12 obtained using the (nonvariational) L2 amplitude density method. The high level of agreement is extremely encouraging because the two methods are totally different in every respect.

The propagation method we use combines the fast fourier transform technique11,12 for evaluating the action of the kinetic energy operator on the wave function and a rotating (body) frame coordinate system,15 which yields a banded kinetic energy and a block diagonal potential matrix. This leads to an algorithm which will scale more slowly than N2, where effectively N is the number of quantum states in the problem.15 This implies that even though the wave packet method may be less efficient than time independent methods for small problems (such as the present example), it will become more efficient as the problem size increases. The calculations presented here are preliminary and in particular used a code which is not fully optimized. Work is in progress to optimize the code, particularly the final state analysis, so that meaningful comparisons of computational effort can be made with time independent methods. The details of the present wave packet formalism will be presented later.21

<table>
<thead>
<tr>
<th>Total E(eV)</th>
<th>Wave packet results</th>
<th>L2-AD results</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>0.31 (- 2)</td>
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</tr>
<tr>
<td>1.20</td>
<td>0.000</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*All results are for total angular momentum J = 0 and for initial state ν = 0, j = 0.

11Results of Zhang et al., Ref. 3.

12For each energy, the upper number is for ν = 0, summed over all final rotational states.

13For each energy, the lower number is for ν = 1, summed over all final rotational states.

14This research supported in part by the Petroleum Research Fund, administered by the American Chemical Society, NASA–AMES Research Center under Grant No. NAG2-503, the Texas Advanced Research Program and the U.S.-Israel Binational Science Foundation.


Electronic spectroscopy of neutral indium phosphide clusters

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(Received 10 February 1989; accepted 8 March 1989)

In this Communication we report the successful application of electronic predissociation and two-color resonant two-photon ionization (R2PI) spectroscopic techniques to the investigation of a broad distribution of small neutral clusters of the important III–V semiconductor, InP. Significant experimental and theoretical effort has been focused on the electronic spectroscopy of neutral dimers and trimers of metal atoms,1–4 as well as dimers and a few tetramers of main group atoms.5–10 Beautiful spectroscopic examinations of some of these systems have been recently reported.10–15 The need exists to develop spectroscopic techniques to expand these studies to significantly larger clusters. We show here that two distinct techniques address this need by providing intense signals for a large distribution of neutral InP clusters.

Electronic behavior of In$_n$P$_m$ clusters is studied using a molecular beam apparatus which employs a source similar to that developed by Smalley and co-workers.1 Clusters are ionized by an F$_2$ (7.88 eV) or ArF (6.42 eV) excimer laser beam (0.2mJ/cm$^2$) transverse to the molecular beam axis, and detected and mass selected using time-of-flight mass spectrometry. A tunable dye laser beam is aligned coaxial with the molecular beam and fires on alternating experimental cycles. Mass spectra are recorded using a transient digitizer interfaced to an averaging memory partitioned for independent averaging of mass spectra obtained alternately with the dye laser on and off.

The electronic predissociation technique relies on the loss of intensity for those InP clusters which absorb a single dye laser photon above their predissociation threshold. The dye laser is fired 100 μs before the ionizing laser to provide ample time for the dissociation process to occur and for the neutral fragment clusters to leave the molecular beam.

Figure 1 contains the results of a predissociation investi-

![Figure 1](image_url)

FIG. 1. Results from the electronic predissociation study of In$_n$P$_m$ clusters showing markedly different dye laser wavelength dependence. Dye laser: 10–20 mJ/cm$^2$; ionizing laser: F$_2$ (7.88 eV), 0.2 mJ/cm$^2$. (a) Mass spectrum recorded in the absence of dye laser pulses; (b), (c) difference mass spectra (dye laser on–dye laser off) recorded with dye laser at 464 and 600 nm, respectively. Positions of In$_n$P$_m$ clusters are marked with horizontal rulings at the top of the figure. Negative-going peaks in the difference spectra represent depletion to cluster signals due to predissociation. Intensity of each mass spectrum is scaled independently.