and the iterations were continued until
\[
\max_r |b_{i+1}(r) - b_i(r)| < 10^{-5},
\]
where \(b_i(r)\) denotes the output of the \(i\)th iteration.

A straightforward application of bipolar coordinates in two dimensions causes the integrand to become singular at all points along the \(r\) axis. This difficulty was avoided by an integration by parts, as suggested by Ben-Naim.\(^3\) The integrations were performed using Simpson's rule with 120 intervals in the range \(0 \leq r \leq 6\sigma\). The criterion for convergence was the same as above, but its magnitude was relaxed to \(10^{-4}\).

The reduced virial pressure \(\rho_v/kT\) and reduced energy \(E/NkT\) were obtained from \(g(r; \rho^*, T^*)\) for various values of \(T^* = kT/\epsilon\) and \(\rho^* = \rho\epsilon^2\) by the usual equations. For the PY case the compressibility pressure \(\rho_v\) was also obtained using the two-dimensional form of Baxter's equation.\(^6\) These calculations are listed in Table I.

Also given in Table I are some molecular-dynamics computer simulations of Fehder,\(^7\) Monte Carlo computer simulations of Tsien and Valleau,\(^8\) and PY calculations of Mandel.\(^5\) We note that our PY and HNC calculations agree only moderately well with the computer simulations, as is the case with the three-dimensional Lennard-Jones fluid. The PY virial and compressibility pressures bracket the computer-simulation pressure for each of the states considered. We also note that our PY results disagree substantially with those of Mandel.\(^5\) Since we obtained identical results using two different procedures for solving the PY equation, we believe that our values in Table I are the correct ones.

A comparison of the PY and HNC radial distribution functions which we obtained with computer simulations and the utilization of these radial distribution functions in a statistical-mechanical perturbation theory will be the subject of a future article.

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lies to the blue of the absorption spectrum. In addition, because the fluorescence spectrum is not much more broadened than the absorption spectrum, pentacene molecules that have undergone one fluorescence cycle cannot be responsible for absorption of the probe beam. Moreover, the intensity of the transient excitation spectrum is found to be proportional to the intensity of the pump beam. Thus we conclude that the transient excitation spectrum corresponds to absorption by $S^1\rightarrow S^0$. This result is reasonable since quantum yield measurements in solution indicate that the fluorescence quantum yield is $8\%$, intersystem crossing $16\%$, and internal conversion $76\%$.

The initial excitation energy of $S_1$ is redistributed among $2.7\times10^{14}$ vibrational levels per wavenumber, preferentially to high-frequency accepting modes such as the symmetric C-H stretch ($=3000 \text{ cm}^{-1}$); and, among others, the symmetric C-C optical mode ($=1400 \text{ cm}^{-1}$). Excitation of the C-H stretch can contribute little to the red shift of the transient excitation spectrum, while the C-C optical mode accounts for "hot bands" in the absorption spectrum (Fig. 2). Clearly, a model in which energy is randomly distributed among the 102 vibrational modes cannot account for the appearance of the observed transient excitation spectrum. Indeed, the red shift requires the preferential population of $v = 2 - 3$ of the C-C optical mode, which evidently does not have sufficient anharmonicity for the vibrational modes to freely exchange energy on the experimental time scale of 1-10 nsec.

These preliminary results demonstrate the ability to follow time evolution of radiationless processes in the collision-free environment of molecular beams. Experiments with improved spectral and temporal resolution should now be possible, as well as comparative studies involving deuterium. Radiationless processes in molecular beams can be used to prepare selectively excited, isolated $S^0$ or $T^1$ molecules in high vibrational states with known energy content so that the subsequent collisional, radiative, and/or intramolecular behavior of these molecules can be studied in a controlled manner.

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**Figure 2.** The absorption spectrum (in the gas phase), the fluorescence spectrum (in solution), and the transient excitation spectrum (in a molecular beam) of pentacene. The arrow points to the wavelength of the pump beam for the transient excitation spectrum.

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