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VIBRATIONAL ENERGY TRANSFER IN BENZENE-ARGON COLLISIONS

by

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ABSTRACT

This paper reports the results of an extensive study of the internal energy-transfer processes that occur in benzene-argon collisions. We used laser-induced fluorescence and information theory for determining the energy-transfer rates between internal states of benzene in the ground electronic state ($^1A_{1g}$). The use of information theory gives estimates for all of the vibrational energy transfer rates. These fit the experimental data reasonably well. However, some of the data do deviate from the information theory model. This suggests that the statistical assumptions of the model are not sufficiently restrictive. One such restriction may be in the number of vibration quantum numbers that change in a collisional event. The rates of vibrational energy transfer depend strongly on the vibrational energy defect.

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The purpose of this study was to measure the rates of vibrational energy transfer in benzene-argon collisions,

where V and V' represent different vibrational states of the $^1\text{A}_{1g}$ (ground) electronic state of the benzene molecule. Reference 1 gives more detailed information on this study. The technique used was laser-induced-fluorescence (LIF) spectroscopy with and without a preceding CO_2 laser pulse. The LIF technique provides an excellent method for measuring changes in vibrational state populations induced by absorption of CO_2 laser radiation and subsequent collisional processes.

For data analysis we used an information-theory approach,²⁻³ where the experimental data constrained the statistical formulation of the rates of energy transfer. The method provides estimates of rate constants for all processes of the type of Eq. (1). The estimated rate constants were consistent with the available data, but they were not necessarily uniquely specified. Additional experimental data would allow one to more precisely determine the rate constants.

The experimental procedure was to measure the intensity of the fluorescence from benzene vapor (in argon diluent) upon excitation with a pulsed ultraviolet laser. In each alternate irradiation a CO_2 laser pulse preceded the uv pulse by 0.5 μs . The intensity of the fluorescence from the $^1\text{B}_{2u}$ electronic state depended on the wavelength of the uv laser and hence, on the population in a given vibrational (and rotational) level of the electronic ground state ($^1\text{A}_{1g}$). The CO_2 laser pulse and molecular collisions both alter the population distribution in the benzene internal states. The change in that distribution as a

function of diluent (argon) pressure is the information that gives the energy-transfer rates. The CO_2 laser frequency was in the spectral region of the ν_{18} absorption band; therefore, those states with non-zero ν_{18} quantum numbers attain the highest population.

The ultraviolet absorption spectrum of benzene [4-5] between 36000 cm^{-1} and 46000 cm^{-1} consists of many discrete vibronic bands that connect the ground electronic state ($^1\text{A}_{1g}$) and the lowest excited single state ($^1\text{B}_{2u}$). We use the nomenclature of Ref 4 for the vibronic transitions. In the example the example $6_0^1 18_1^1$, the ν_6 quantum number is 0 in the $^1\text{A}_{1g}$ state and 1 in the $^1\text{B}_{2u}$ state. The ν_{18} quantum number is 1 in both states. All other vibrational quantum numbers are zero in both states.

Figure 1 shows a schematic diagram of the experimental apparatus, and Table 1 summarizes the experimental conditions. Computers controlled both the laser operation and the data acquisition.

The experimental data were of two types: uv frequency scans at constant benzene and argon partial pressures (Figs. 2,3), and argon pressure scans at a constant uv frequency and benzene partial pressure. Each scan gave the fluorescence-excitation signal with and without the CO_2 laser. From these signals we obtained the changes induced by the CO_2 laser in the population of different vibrational levels. Figures 4 and 5 summarize these changes for several vibrational levels at 20-mbar total pressure, and Figs. 6-8 show the pressure dependence (argon) for three vibrational state populations. These data are all for 0.08-mbar benzene. The population change is $N(V)/N_0(V)$, where $N(V)$ is the population of vibrational level V after the $0.5\text{ }\mu\text{s}$ delay. The zero subscript indicates the population in the sample without excitation by infrared radiation. The energy scale (abscissa) in Figs. 4 and 5 is the energy of the vibrational states. The squares with error bars are the experimental values

and the small dots are the model calculations (also explained below). Figure 4 shows the population changes for states with $v_{1g} \neq 0$, and Fig. 5 shows the changes with $v_{1g} = 0$. The points in Figs. 6-8 are the experimental data, and the solid curves are model calculations.

The model is a set of differential equations that describes the flow of population among the vibrational and rotational states of benzene vapor. The population-transfer processes are collisional transfer of rotational energy, collisional transfer of vibrational energy, and absorption and emission of infrared radiation. Table 2 gives the important features of the model.

The processes that change the vibrational state of the benzene molecule are of two types: collisional and radiative processes. The quantities σ and $I(t)$ in the radiative part of the rate constant matrix (Table 2) are, respectively, the benzene absorption cross section for the CO_2 laser and the intensity profile of the laser pulse. The quantity k_c in the collisional part of the matrix is the rate constant for hard sphere collisions.

The collisional processes are of two types: rotational energy transfer and vibrational energy transfer. The major role of rotational energy transfer is to change the molecule from rotational states that do not absorb the CO_2 laser to those that do. The fraction of molecules initially in absorbing rotational states depends somewhat on the vibrational state. That fraction was an adjustable parameter in fitting the experimental results. The derived fraction was between 0.5 and 1.0% for the states of interest.

The vibrational energy transfer plays a major role in the experiments. We used an information theory approach as outlined in Table 2 to estimate those rates. The two adjustable parameters, λ_0 and λ_1 , provide most of the adjustment necessary to fit the experimental data. The values we obtained were

$$\lambda_0 = 7.50$$

$$\lambda_1 = 3.20 \quad .$$

The final adjustment to the model was an indirect restriction on the number of vibrational quantum numbers that change per collision. The adjustment was mainly a restriction on the total rate of energy transfer from a single state. The small dots in Figs. 2 and 3 and the solid lines in Figs. 4-6 are the model predictions for the experiment. The agreement with the experiment was good.

Table 3 gives some representative rate constants that follow from the fitting procedure. The values in the table are predictions of the model and not direct measurements of the stated rates. The processes that are most sensitive to the experimental data are those involving the ν_{18} mode. The first three entries are nearly completely insensitive to the vibrational energy transfer rates. (They depend strongly, however, on the rotational relaxation rate and the fraction of molecules in absorbing states.) We have included them to show the model predictions.

In summary, the laser-induced fluorescence technique provides an excellent method for monitoring the rates of vibrational energy transfer in the ground electronic state of species like benzene. By varying the pressure of an argon diluent, we obtained information that allowed us to estimate the rates of vibrational energy transfer in argon-benzene collisions. The information-theory technique provided a good method for estimating all of the vibrational rates. The results confirm that the transfer rate depends strongly on the energy defect and gave a measure of that dependence. Additional restrictions, such as those on the number of vibrational quantum numbers changing per collision, may also be important.

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EXPERIMENTAL CONDITIONS

- INFRARED LASER = PULSED CO₂
1037.43 cm⁻¹, 3.6 J/cm²
- ULTRAVIOLET LASER = KrF-PUMPED DYE LASER, DOUBLED
259–277 nm, 2–20 mJ/cm²
- FLUORESCING ELECTRONIC STATE = ¹B_{2u}
- BENZENE PRESSURE = 0.08 mbar
- ARGON PRESSURE = 0–100 mbar
- TIME DELAY BETWEEN LASERS = 0.5 μs

RATES OF VIBRATIONAL ENERGY TRANSFER ESTIMATED BY USING INFORMATION THEORY TO FIT THE EXPERIMENTAL DATA

RATE EQUATIONS IN VECTOR FORMAT:

$$\dot{\mathbf{N}} = \mathbf{A}\mathbf{N}$$

$\mathbf{N}$ = VECTOR WHOSE ELEMENTS ARE LEVEL POPULATIONS

$\mathbf{A}$ = RATE CONSTANT MATRIX WITH COLLISIONAL AND RADIATIVE PARTS

$$\mathbf{A} = k_c \rho_M \mathbf{P} + (\sigma I(t)/h\nu) \mathbf{F}$$

$\mathbf{P}$ = MATRIX WHOSE ELEMENTS, p_{ij} , ARE PROBABILITIES OF COLLISIONAL TRANSFER FROM STATE j TO i

$\mathbf{F}$ = SIMILAR MATRIX FOR RADIATIVE PROCESSES

$p_{ij} = k(V \rightarrow V')/k_c$ WHEN i AND j INDEX DIFFERENT VIBRATIONAL STATES

$k(V \rightarrow V')$ = INFORMATION THEORY RATE CONSTANT

$$k(V \rightarrow V') = k_0(V \rightarrow V') \exp(-\lambda_0 - \lambda_1 |E_V - E_{V'}|/kT)$$

$k_0(V \rightarrow V')$ = STATISTICAL ESTIMATE (PRIOR) OF THE RATE CONSTANT,
PROPORTIONAL TO THE NUMBER OF FINAL STATES
(INCLUDING TRANSLATIONAL)

λ_0, λ_1 = ADJUSTABLE PARAMETERS

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TABLE 3
RATE CONSTANTS DERIVED FROM EXPERIMENTAL DATA^a

<u>V</u>	<u>V'</u>	<u>k(V → V')</u> <u>(cm³ molec⁻¹ s⁻¹)</u>	<u>E_V - E_{V'}</u> <u>(cm⁻¹)</u>	<u>G'</u>
16 ₁	0 ₀	9.9x10 ⁻¹⁶	398.8	1
6 ₁	16 ₁	3.0x10 ⁻¹⁴	209.5	2
6 ₁	0 ₀	4.5x10 ⁻¹⁷	608.3	1
18 ₁	6 ₁ 16 ₁	6.3x10 ⁻¹³	29.9	4
18 ₁	1 ₁	2.7x10 ⁻¹³	43.9	1
18 ₂	6 ₁ 16 ₁ 18 ₁	3.8x10 ⁻¹³	29.9	8
18 ₂	1 ₁ 18 ₁	1.6x10 ⁻¹³	43.9	2
18 ₁	All ^b	2.1x10 ⁻¹²	---	--
18 ₂	All ^b	7.9x10 ⁻¹²	---	--

^a From fit to model

^b Sum of rate constants into all final states.

Figure Captions

1. Schematic diagram of experimental apparatus.
2. Laser-induced fluorescence (LIF) spectrum in the region of 38480 cm^{-1} with and without CO_2 -laser pulses for 0.08 mbar benzene diluted with argon to 20 mbar.
3. LIF spectrum in the region of 37500 cm^{-1} with frequencies marked for typical pressure scans. The gas sample was the same as Fig. 2.
4. Population of level V relative to the thermal population at $0.5\text{ }\mu\text{s}$ after the CO_2 laser pulse for a total pressure of 18-20 mbar (0.08 mbar benzene). All points are for states with some excitation in the ν_{18} mode. The squares with error bars are the experimental data (from spectra like Figs. 2-3) and the small dots are the model predictions. Vibrational levels in this figure are 18_1 , 16_118_1 , 6_118_1 , 16_218_1 , 1_118_1 , $6_116_118_1$, 18_2 , and 6_218_1 .
5. Same as Fig. 6 for levels with no ν_{18} quanta. Vibrational levels are: 0_0 , 16_1 , 6_1 , 16_2 , 10_1 , 1_1 , 6_116_1 , 6_2 , 6_111_1 , 16_11_1 , 6_116_2 , 6_110_1 , 6_216_1 , and 6_216_2 . Note the change in vertical scale.
6. Relative change of population of vibrational level 0_0 versus pressure. The symbols are experimental results (from data like Fig. 5), and the solid curve is the model prediction. The diluent is argon; P_B is the partial pressure of benzene, and $N_0(0_0)$ is the density of molecules in level 0_0 at thermal equilibrium.
7. Relative change of population of level 6_116_1 versus pressure.
8. Relative change of population of level 18_1 versus pressure.

Figure 2

Figure 3

Figure 6

Figure 7

Figure 8

Figure 11

Figure 12