# Vibrational Relaxation of Highly Excited Toluene in Collisions with He, Ar, and $N_2$ at Temperatures down to 38 K[†]

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We report the first low temperature measurements on the collisional relaxation of toluene molecules initially containing high amounts of internal excitation. These highly excited toluene molecules are generated by photoisomerization of cycloheptatriene molecules that are excited by irradiation with the output of an excimer laser operating at 248 nm. These measurements have been performed on very dilute mixtures of cycloheptatriene in He, Ar, or $N_2$ carrier gas in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus. Collisional relaxation of the excited toluene molecules is followed by observing their time-resolved infrared fluorescence. Analysis of the results allows us to infer how the average energy removed per collision, $\langle\langle \Delta E \rangle\rangle$, varies with the average energy contained in the toluene molecule, $\langle\langle E \rangle\rangle$, for toluene−He collisions down to 38 K, for toluene−Ar collisions down to 112 K, and for toluene−$N_2$ collisions down to 74 K. In no case is the variation of $\langle\langle \Delta E \rangle\rangle$ with temperature strong. However, in the case of toluene−He, the trend is for $\langle\langle \Delta E \rangle\rangle$ to decline with temperature, whereas for toluene−Ar and toluene−$N_2$ $\langle\langle \Delta E \rangle\rangle$ is essentially independent of temperature. It is suggested that these results may reflect the relative influence of the van der Waals forces in inducing energy transfer.

## 1. Introduction

The technique of time-resolved, laser-induced, infrared fluorescence has served for over 30 years in investigations of collision-induced vibrational energy transfer. The method was first developed by Brad Moore[1] (and independently by Javan, Flynn and co-workers[2]) shortly after the first reports of the development of pulsed infrared lasers. At first, it was applied to studies of the relaxation of small molecules (e.g., $CO_2$, HF, HCl, and CO)[2b,3] from low levels of vibrational excitation. More recently, this general technique has been extended in two main ways. First, the development of tuneable laser sources[4] and Raman-pumping[5] techniques has allowed experiments to be performed on a wider range of molecules and molecular energy levels than was possible previously. Second, techniques other than vibrational fluorescence, especially laser-induced fluorescence in double-resonance experiments,[6] have been developed to observe the fate of the molecules that are excited by the laser pulse.

Another important development was pioneered by Barker and co-workers.[7,9−12] They have used the observation of time-resolved infrared fluorescence (TR-IRF) to follow the collision-induced vibrational relaxation of large molecules from high levels of vibrational excitation. Among the molecules that they have studied are azulene,[8] pyrazine,[9] toluene,[10] and benzene.[11] In contrast to the experiments on small molecules at low levels of excitation, these aromatic molecules are not excited directly within their $S_0$ electronic ground state. Rather, one relies on their photophysical properties. Excitation to an excited electronic state, usually $S_1$, by irradiation with a pulsed laser must be followed by rapid radiationless conversion back to the $S_0$ state, by either internal conversion or successive processes of intersystem crossing, so that molecules are created with a high, and rather well-defined, vibrational energy. Fluorescence is observed from the high frequency fundamental modes (usually the C−H stretching vibrations), and the TR-IRF signals are interpreted on the basis that intramolecular relaxation is essentially complete and instantaneous, so that the relationship between the intensity of the observed emission and the internal energy content[8b] can be determined via an expression first derived by Durana and McDonald,[12] which is closely related to those used in RRKM treatments of unimolecular reactions.[13] Using this analysis, it is possible to derive values of the mean energy removed per collision, $\langle\langle \Delta E \rangle\rangle$, at each value of the mean vibrational energy content, $\langle\langle E \rangle\rangle$, for all energies less than that initially deposited in the molecule by the photoexcitation process. (The double brackets, $\langle\langle\ \rangle\rangle$, imply averaging: in the case of $\Delta E$, over the distributions of internal energies and of $\Delta E$ values; in the case $E$, over both the thermal distribution of collision energies and the distribution of the internal energies $E$ which broadens as the excited molecules relax.) In contrast to the experiments on small molecules at low levels of excitation, no information is gained at the state-to-state level, nor does one learn from which modes energy is removed (as far as it is possible to refer to separable modes at the state densities present in these experiments).

As long as the photophysical properties of the molecule are suitable, TR-IRF experiments are straightforward to implement and information has been gathered for relaxation by a large range of colliding gases (M), varying in size from the noble gas atoms to polyatomic molecules as large as the “parent” molecules themselves. Two general conclusions have emerged. First, the value of $\langle\langle \Delta E \rangle\rangle$ increases as the size (i.e., the number of atoms) of M increases. Second, the values of $\langle\langle \Delta E \rangle\rangle$ increase, very approximately linearly, with $\langle\langle E \rangle\rangle$.

For a time, the second of these conclusions was controversial. Troe and co-workers[14,15] have carried out experiments parallel to those of Barker’s group. The two groups have usually

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employed the same methods of laser excitation but, in Troe's experiments, relaxation of the vibrationally excited molecules was normally monitored by making time-resolved measurements on the ultraviolet absorption (TR-UVA) of the excited molecules. Their method is calibrated by making similar spectroscopic measurements on the UVA of shock-heated or laser-heated gas. They concluded from their early relaxation measurements[15a,b,16a] that $\langle\langle \Delta E \rangle\rangle$ was essentially independent of $\langle\langle E \rangle\rangle$.

A further, elegant, technique for measuring rates of collisional energy transfer from highly excited aromatic molecules has been developed in Göttingen by Luther and co-workers.[16,17] Again, the excited molecules whose relaxation is to be studied are created by electronic excitation followed by radiationless return to the $S_0$ state. However, relaxing molecules are now observed using the technique of time-resolved, kinetically controlled selective ionization (TR-KCSI), in which molecules within a narrow band of internal energies are selectively ionized using a pulsed dye laser. The method not only provides accurate values for $\langle\langle \Delta E \rangle\rangle$ but also information about the form of the probability function $P(E',E)$ which describes the distribution of final internal energies $E'$ produced when molecules with internal energy $E$ undergo collisions. Measurements on toluene and azulene confirmed the dependence of $\langle\langle \Delta E \rangle\rangle$ on $\langle\langle E \rangle\rangle$, and the proposal has been made[16] that the early TR-UVA data that suggested otherwise depended strongly on a particular point in the calibration of UVA with internal energy. Further experiments[15c] using the TR-UVA method to study the relaxation of azulene molecules created with lower initial energies appear to confirm this conclusion.

Very recently Luther and co-workers[17] have described the TR-KCSI method in detail and reported extensive results for the collisional relaxation of toluene formed by the photoisomerization of cycloheptatriene at 266 nm. In these experiments, it has been possible not only to determine $\langle\langle \Delta E \rangle\rangle$ versus $\langle\langle E \rangle\rangle$ curves but also to find the form of the probability functions $P(E',E)$ for several collision partners and a wide range of internal energies. Such measurements represent an important step forward in our understanding of collisional energy transfer in large, highly excited molecules and provide a new test for the theory of such processes.

Up to the present time, theoretical work on the vibrational relaxation of highly excited aromatic molecules has largely made use of the classical trajectory technique.[18] In the most recent work, and that of some relevance to the results that are reported here, Lenzer and Luther[19] have investigated how the values of $\langle\langle \Delta E \rangle\rangle$ for collisions between excited benzene and noble gases depend on the form used for the intermolecular potentials, particularly the well depths. When agreement was found with the absolute magnitudes of $\langle\langle \Delta E \rangle\rangle$ derived from experiment, the values of $\langle\langle \Delta E \rangle\rangle$ were found to increase with $E$ in the manner now generally agreed between the experimentalists.

So far there have been few efforts to investigate the *temperature dependence* of vibrational relaxation from high levels of excitation in large molecules. In particular, only in recent experiments by Miller et al.[10b] on pyrazine self-relaxation between 254 and 414 K have experiments been carried out below room temperature. The results showed that $\langle\langle \Delta E \rangle\rangle$ was essentially constant at room temperature and above but started to increase below 300 K. This lack of low-temperature data contrasts with the situation for diatomic molecules. For example, experiments on the self-relaxation of HCl($v = 1$),[20] the self-relaxation of NO($v = 3$),[21] and the relaxation of CO($v = 1$) by He and $D_2$ [22] have all shown how weak intermolecular attraction can enhance the rates of energy transfer at low temperatures.

The aim of the work that is reported here was to make the first measurements on collisional energy transfer from highly excited polyatomic molecules at very low temperatures. For this purpose, we have utilized our CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus.[23] The CRESU method, originally devised by Rowe and co-workers,[24] employs expansion through a Laval nozzle to generate a supersonic flow of moderately dense gas at a defined temperature. The speed of the flow and the lack of contact with cooled surfaces ensure that highly supersaturated conditions can be reached, and the method has been applied to a range of elementary molecular processes.[21,25]

In the present experiments, small flows of cycloheptatriene (CHT) were injected into the carrier gas (He, Ar, or $N_2$), giving a CHT mole fraction of ca. $(1-4) \times 10^{-3}$. The amount was limited by the difficulty of introducing the vapor of a rather involatile species into the very large gas flows that are necessarily present in the CRESU apparatus. CHT was excited by the output at 248 nm of an excimer laser operating on KrF. Excited at this energy, CHT undergoes rapid radiationless transfer to its electronic ground state followed by rapid isomerization to toluene.[26,27] This method of generating highly vibrationally excited CHT has been employed in a number of studies of collisional energy transfer using the TR-UVA technique.[16]

We observed TR-IRF in transitions of the C−H stretching modes of the vibrationally excited toluene molecules. Because of the very low mole fractions of CHT present, the information obtained was restricted to collisions between excited toluene molecules and $N_2$, Ar, and He. We chose to use photoexcitation of CHT to generate highly excited toluene because (i) the vapor pressure of CHT made it possible to introduce sufficient aromatic compound into the high gas flow in the CRESU apparatus, and (ii) CHT has a higher absorption cross section than toluene itself at the laser wavelength of 248 nm.[28]

## 2. Experimental Section

A detailed description of the CRESU method, which permits kinetic measurements at temperatures as low as 7 K in some cases,[21,23b] has been given by Sims et al.[29] Full specifications of the CRESU apparatus used in the present experiments has also been given recently.[23b] Here, we concentrate on those features of our experiments that are specific to the present measurements.

The heart of the CRESU apparatus is an axisymmetric Laval nozzle. It is mounted on a reservoir which is equipped with a perforated Teflon disk to ensure laminar flow and good mixing of the gas streams entering the reservoir. Low temperatures are achieved in the gas flows by isentropic expansion of the gas mixture prepared in the reservoir through the nozzle and into the main chamber. A supersonic flow of gas is generated in which the Mach number, the temperature, the density of the gas, the mole fractions of the components, and the velocity of the gas stream are constant along the axis of the flow. Several nozzles were employed in the present work, each providing a particular temperature and density for the selected carrier gas: $N_2$, Ar, or He. All of the nozzles had been characterized by impact-pressure measurements, and the temperatures provided by some nozzles have been confirmed spectroscopically.[16c,23]

The total flow of gas through the CRESU apparatus is typically in the range 40−50 slm (standard liters per minute). This requires a large pumping system (Pfeiffer Vacuum; ca.

30 300 $m^3$ $hr^{-1}$ for He), consisting of three stages of Roots pumps backed by a large rotary pump.[23] The flow of carrier gas is controlled by a calibrated 100 slm mass flow controller (MKS). In the present experiments, the large gas flows presented difficulties in introducing sufficient concentration of CHT to generate easily observable IRF signals. On the other hand, the small mole fractions of CHT introduced two simplifications to our experiments and their interpretation: first, we could neglect any effects due to dimerization and subsequent condensation of the CHT, and, second, the relaxation of excited toluene is dominated by collisions with the carrier gas. Both of these points are discussed further below.

A flow of CHT was admitted to the gas reservoir using a flow line which was separate from that for the main flow of carrier gas and which incorporated a "bubbler system". It consisted of a 250 $cm^3$ round-bottomed flask holding CHT through which carrier gas was bubbled. This flow was controlled by a 2 slm mass flow controller (MKS). The flask was immersed in a water bath at ca. 23 °C. Downstream from the flask, this gas flow passed through a trap held at ca. 18 °C. This arrangement ensured that the gas flow exiting the trap contained a mole fraction of CHT corresponding to its vapor pressure at 18 °C. Knowledge of this vapor pressure, the pressure in this flow line, and the monitored flows of gas made it possible to estimate the mole fraction of CHT in the total flow (see below, Table 3).

CHT molecules in the CRESU flow were excited with the 248 nm output from a KrF excimer laser with unstable resonator optics (Lambda-Physik, Compex 102) operating at 10 Hz. The laser beam propagated through the gas reservoir and the throat of the Laval nozzle and then along the axis of the supersonic gas flow. At the exit of the nozzle, the laser beam was estimated to have a diameter of approximately 0.7 cm and a fluence of approximately 50 mJ $cm^{-2}$. IRF signals from excited toluene molecules were observed at a point approximately 10 cm downstream from the exit of the Laval nozzle using a liquid-$N_2$-cooled InSb photoconductive detector, with a 4 mm square element, mounted above the gas flow. Emission signals were enhanced through the use of a gold-coated "collecting" mirror (75 mm diameter, 75 mm focal length), which was placed below the flow and positioned so as to gather IRF and focus it onto the detector element. The detector and mirror were mounted in the main CRESU chamber, but the supersonic flow could pass between them undisturbed. The detector was provided with a custom-built amplifier and the combined response time was set, typically to 1−2 $\mu$s, to optimize the signal-to-noise ratio on the IRF traces but to be sufficiently short so as not to distort the IRF decays. Signals from the amplifier were passed to a digital storage oscilloscope (LeCroy 9300 series) and from there to a PC. Typically, signals from 20 000 laser shots were accumulated for subsequent fitting.

In addition to experiments at low temperatures, two sets of measurements were performed at room temperature for each collider gas used in the CRESU experiments (i.e., He, Ar, and $N_2$). They were carried out in conventional "slow flow" mode, using a small Pyrex cell (40 cm long, 2.5 cm diameter), and were very similar to those conducted by Barker and co-workers.[8−12] In one set, toluene was excited directly using the frequency-quadrupled output from a Nd:YAG laser at 266 nm. In the second set, photoisomerization of CHT was again used to generate highly excited toluene, but photoexcitation was via irradiation with the 308 nm output from an XeCl excimer laser (Lumonics, HyperEx 400). The same combination of detector, amplifier, and PC was used to acquire and store signals as in the CRESU experiments. However, in this case no collecting optics were employed, IRF was observed by placing the liquid-$N_2$-cooled InSb detector as close as possible to a sapphire window on the side of the cell.

Greater variation in gas mixtures was possible in the cell experiments. Gas mixtures of toluene and collider gas, or CHT and collider gas, were prepared in Pyrex storage bulbs and then flowed slowly through the cell while TR-IRF signals were collected, typically from 1000 laser shots. For a given prepared mixture, IRF decays were recorded for several total gas pressures in the cell. The higher absolute concentrations of toluene or CHT in these experiments, compared with those of CHT in experiments in the CRESU apparatus, meant that the IRF traces were of higher quality.

## 3. Analysis

The method used to convert the observed TR-IRF signals to curves of $\langle\langle \Delta E\rangle\rangle$ against $\langle\langle E\rangle\rangle$ closely follows that developed by Barker and co-workers.[8−12] As they have described this method in detail on several occasions, we give a concise, but self-contained, description. The principal assumptions behind the analysis are as follows. First, intramolecular vibrational energy redistribution is complete and rapid compared with the time scale of collisional relaxation, so that the intensity of the observed IRF emission, which is associated with transitions between levels differing in the number of quanta in the C−H stretching modes, reflects the total vibrational energy content of the excited molecules. Second, the relationship between the intensity of the observed IRF, $I_{IRF}$, and the vibrational energy content, $E$, which is derived on the basis of a statistical distribution of $E$ over the normal modes of the molecule, is not distorted appreciably by the spreading of $E$ that occurs as the ensemble of excited molecules undergoes collisional relaxation. Third, despite the high energies of excitation, because the average energy per mode is not too great, formulas based on the assumption of harmonic vibrations will be adequate.

To relate $I_{IRF}$ to $E$, use was made of the expression originally employed by Durana and McDonald[13]

$$I_{IRF}(E) = \frac{N_{ex}}{\rho_s(E)} \sum_{i=1}^{\text{modes}} h\nu_i A_i^{1,0} \sum_{v_1=1}^{v_{max}} v_i \rho_{s-1}(E - v_i h\nu_i) \qquad \text{(i)}$$

where $N_{ex}$ is the concentration of excited molecules, $A_i^{1,0}$ is the spontaneous emission coefficient for the 1,0 transition of mode $i$, $v_i$ is the quantum number in this mode and $h\nu_i$ the energy of the emitted photon, and $\rho_s(E)$, and $\rho_{s-1}(E - v_i h\nu_i)$ are, respectively, the density of states for all $s$ oscillators at energy $E$ and that for $s-1$ modes when energy equal to $v_i h\nu_i$ is present in the emitting mode.

In practice, the observed emission intensity, $I_{IRF}$, is only from transitions associated with the C−H stretching modes and absolute emission intensities are not observed. Consequently, the terms $N_{ex}$, $h\nu_i$ and $A_i^{1,0}$ can be collected into a constant term and the observed emission intensity $I_{IRF}(E)$ can be related simply to the densities of states by the expression

$$I_{IRF}(E) = \frac{1}{\rho_s(E)} \sum_{i=1}^{\text{modes}} \sum_{v_1=1}^{v_{max}} v_i \rho_{s-1}(E - v_i h\nu_i) \qquad \text{(ii)}$$

To convert the decays of $I_{IRF}(E)$ to decays in the (mean) vibrational energy of the excited molecules, Toselli et al.[11] scaled their experimental signals so that the value at zero time corresponded to the value of 0.177 given by evaluating eq (ii).

At our higher initial energy of 51 850 cm$^{-1}$, it was necessary to use a different scaling factor, $I_{\mathrm{IRF}}{}^0(E) = 0.26$. With this change, it was then possible to use the equation relating $I_{\mathrm{IRF}}(E)$ to $(E)$ derived by Toselli et al.[11]

$$\ln E = 11.9241 + 0.8970 \ln I_{\mathrm{IRF}} + 0.0932(\ln I_{\mathrm{IRF}})^2 + 0.00640(\ln I_{\mathrm{IRF}})^3 + 0.00023\,(\ln I_{\mathrm{IRF}})^4 \quad \text{(iii)}$$

Like Barker and co-workers, we do not use eq (iii) to convert the value of $I_{\mathrm{IRF}}$ at each delay time to a corresponding value of $E$. Instead, we first fit the traces of $I_{\mathrm{IRF}}$ versus time to the functional form

$$I_{\mathrm{IRF}}(t) = I^0_{\mathrm{IRF}} \exp(-k't - b't^2) \quad \text{(iv)}$$

However, rather than use the parametrized form for $I_{\mathrm{IRF}}(t)$ in eq (iv) to find how $E$, or strictly the ensemble average $\langle\langle E\rangle\rangle$, varies with time, the dependence on time is transformed to dependence on the average number of collisions, $Z$, undergone by an excited molecule by a given time, using the equation

$$Z = k_{\mathrm{LJ}} N t \quad \text{(v)}$$

where $k_{\mathrm{LJ}}$ is the rate constant for bimolecular collisions between the vibrationally excited species (toluene in our experiments) and a gas at concentration $N$.[a] (The case where parent−parent collisions are also important requires an extended treatment, which is described below.) Then the decays of IRF intensities can be expressed as

$$I_{\mathrm{IRF}}(t) = I^0_{\mathrm{IRF}} \exp(-kZ - bZ^2) \quad \text{(vi)}$$

and the derived values of $k$ and $b$ should be independent of the total pressure of the gas mixture for a particular parent−collider composition.

Now eqs (iii) and (vi) can be combined to give the variation of $\langle\langle \mathrm{E}\rangle\rangle$ with $Z$ in terms of $k$ and $b$. Furthermore, if that expression is differentiated with respect to $Z$, then

$$\mathrm{d}\langle\langle E\rangle\rangle/\mathrm{d}Z = \langle\langle \Delta E\rangle\rangle \quad \text{(vii)}$$

Consequently, the variation of $\langle\langle \Delta E\rangle\rangle$ with $\langle\langle E\rangle\rangle$ can be extracted.

To facilitate comparison of our results with earlier data, in calculating $k_{\mathrm{LJ}}$ we have used the Lennard-Jones parameters tabulated by Toselli et al.,[11] and before that by Hippler et al.[16b,c] Values of the collision integral $\Omega_{(2,2)}{}^*$ were evaluated using the approximate formulas of Troe.[30] The resultant values of $k_{\mathrm{LJ}}$ for toluene−collider collisions are given in Table 3.

As mentioned above and discussed below, in the low temperature CRESU experiments, collisions between excited toluene molecules and CHT have been ignored, on account of the very low mole fractions of CHT in the supersonic flows, and relaxation is assumed to occur entirely as a result of collisions with the carrier or collider gas. In our room-temperature cell experiments, however, measurements were carried out on much "richer" gas mixtures and it was necessary to allow for relaxation by collisions with both CHT and M. Again we followed methods established by Barker and co-workers. The values of $k$ and $b$ determined from a set of measurements, on a gas mixture of particular composition but at different total pressures, were plotted against the parameter $F_{\mathrm{M}}$ defined by

$$F_{\mathrm{M}} = \frac{N_{\mathrm{M}}\, k^{\mathrm{M}}_{\mathrm{LJ}}}{N_{\mathrm{M}}\, k^{\mathrm{M}}_{\mathrm{LJ}} + N_{\mathrm{CHT}}\, k^{\mathrm{CHT}}_{\mathrm{LJ}}} \quad \text{(viii)}$$

where $k^{\mathrm{M}}_{\mathrm{LJ}}$ and $k^{\mathrm{CHT}}_{\mathrm{LJ}}$ are the rate constants for collisions between excited toluene and M and between excited toluene and CHT, and $N_{\mathrm{M}}$ and $N_{\mathrm{CHT}}$ are the concentrations of M and of CHT, respectively. The experimental measurements at each $F_{\mathrm{M}}$ were then fitted to a quadratic expression to find the values of $k$ and $b$ at $F_{\mathrm{M}} = 0$ (i.e., for toluene−toluene or toluene−CHT collisions) and $F_{\mathrm{M}} = 0$ (i.e., for toluene−M collisions). These values of $k$ and $b$ were then used to extract curves for collisions of excited toluene with CHT, He, Ar, and $N_2$ at room temperature.

## 4. Results

**(a) Room-Temperature Experiments.** Two sets of experiments were performed in the small, room-temperature cell to determine curves of $\langle\langle \Delta E\rangle\rangle$ versus $\langle\langle E\rangle\rangle$ for collisions between highly excited toluene molecules and He, Ar, and $N_2$. In the first set, toluene vapor, pure or diluted in one of these gases, was excited with the frequency-quadrupled output of a Nd:YAG laser operating at 266 nm, thereby producing molecules with ca. 38 300 cm$^{-1}$ initial energy. In the second set, as in the low-temperature experiments, excited toluene was formed via the photoisomerization of CHT, but in this case the CHT was excited at 308 nm using the output of an excimer laser operating on XeCl. This produced toluene molecules with an initial energy equivalent to ca. 44 000 cm$^{-1}$.

In both sets of experiments, traces of TR-IRF were recorded from samples of the pure parent (toluene or CHT) and from mixtures of these gases diluted in He, Ar, and $N_2$. In measurements on pure "parent", the pressure was varied between 10 and 50 mTorr in 10 mTorr increments. In diluted mixtures, total pressures were used containing the same partial pressures of parent as in the pure samples that were studied.

In general, the traces of TR-IRF were fitted to the form given in eq (iv). However, for experiments involving direct excitation of toluene at 266 nm, it was found that a simple exponential function (i.e., with $b = 0$ in eq (iv)) provided as good a fit to the traces as the more complicated function. The parameters $k'$ (in $\mu$s$^{-1}$) and $b'$ (in $\mu$s$^{-2}$) were then converted to values of $k$ and $b$ (see eq (vi)). Each experiment on a mixture of the same parent−collider composition then yielded values of $k$ and $b$ that should be identical. In practice, the values of $k$ and $b$ in each such set of experiments showed more scatter than the errors returned from fitting the individual TR-IRF traces. Consequently, we took a simple average of the five values of $k$ and $b$ for mixtures of the same composition but different total pressure and used the standard deviations in these values as the errors for subsequent use.

To estimate values of $k$ and $b$ for collisions of excited toluene with pure collider, we fitted the values of $k$ and $b$ for mixtures of different composition involving the same parent and collider to a quadratic function in $F_{\mathrm{M}}$ (see eq (viii)). This procedure yielded the results shown in Table 1. Because the number of points used to establish the quadratic fits was not much larger than the number of parameters in the fitting expression, the errors in the values of $k$ and $b$ in the pure collider limit ($F_{\mathrm{M}} = 1$) were taken to be the standard deviation of the measured values from the fitted values for those mixtures with $F_{\mathrm{M}} \geq 0.9$. Usually four measurements were made in this range.

Having obtained values of $k$ and $b$ for individual parent−collider pairs, the variation of $\langle\langle \Delta E\rangle\rangle$ with $\langle\langle E\rangle\rangle$ could be

**TABLE 1: Values of $k/(10^{-2}Z)^{-1}$ and $b/(10^{-2}Z)^{-2}$ Obtained From the Analysis of Room Temperature Experiments**

| experiment | $k/(10^{-2}\,Z)^{-1}$ | $b/(10^{-2}\,Z)^{-2}$ |
|---|---|---|
| Direct Excitation of Toluene at 266 nm | | |
| toluene*−toluene | 5.2 ± 0.7[a] | |
| toluene*−He | 0.36 ± 0.08 | |
| toluene*−Ar | 0.92 ± 0.23 | |
| toluene*−$N_2$ | 1.30 ± 0.16 | |
| Excitation of Toluene via Photoisomerization of CHT Excited at 308 nm | | |
| toluene*−CHT | 3.6 ± 0.3 | 7.9 ± 1.3 |
| toluene*−He | 0.22 ± 0.07 | 0.07 ± 0.16 |
| toluene*−Ar | 0.67 ± 0.09 | 0.18 ± 0.01 |
| toluene*−$N_2$ | 0.47 ± 0.04 | 0.28 ± 0.02 |

[a] The estimate of the errors is described in the text.

**TABLE 2: Comparison of $\langle\langle\Delta E\rangle\rangle$ Values at $\langle\langle E\rangle\rangle = 24\,000$ cm$^{-1}$: (a) Derived From Experiments Employing Direct Excitation of Toluene at 266 nm; (b) Derived From Experiments Employing Excitation of Toluene Via Photoisomerization of CHT Excited at 308 nm; and (c) From Ref 11**

| | (a) $\langle\langle\Delta E\rangle\rangle$ $E_{\text{initial}}$ = 38 100 cm$^{-1}$ | (b) $\langle\langle\Delta E\rangle\rangle$ $E_{\text{initial}}$ = 44 000 cm$^{-1}$ | (c) $\langle\langle\Delta E\rangle\rangle$ $E_{\text{initial}}$ = 40 8000 cm$^{-1}$ |
|---|---|---|---|
| toluene*−toluene | 650 ± 30 | | 867 ± 18 |
| toluene*−CHT | | 860 ± 63 | |
| toluene*−He | 45 ± 4 | 70 ± 18 | 62 ± 1 |
| toluene*−Ar | 115 ± 11 | 131 ± 19 | 112 ± 3 |
| toluene*−$N_2$ | 161 ± 9 | 147 ± 10 | 139 ± 4 |

estimated using eqs (iii), (vi), and (vii) given above. Curves of $\langle\langle\Delta E\rangle\rangle$ versus $\langle\langle E\rangle\rangle$ are displayed in Figure 1 for toluene colliding with He, Ar, and $N_2$ at room temperature. The two sets are derived from the two sets of experiments: those employing direct excitation of toluene at 266 nm, and those in which toluene is formed via photoisomerization of CHT induced at 308 nm. The values of $\langle\langle\Delta E\rangle\rangle$ for $\langle\langle E\rangle\rangle = 24\,000$ cm$^{-1}$ derived from our two sets of experiments are compared in Table 2 with those determined by Barker and co-workers.[11]

**(b) Low-Temperature CRESU Experiments.** For reasons explained earlier, in all of the low temperature measurements, toluene molecules with large amounts of vibrational energy were generated by photoisomerization of CHT excited at 248 nm, rather than by direct excitation of toluene. The excited molecules therefore initially contained ca. 51 900 cm$^{-1}$ initial energy, this comprising the sum of the photon energy (40 320 cm$^{-1}$), the energy of isomerization (11 090 cm$^{-1}$), and the initial vibrational energy of the CHT molecules (475 cm$^{-1}$), assumed to be unrelaxed during the expansion. The nature of the CRESU experiments also imposed two limitations not present in the room-temperature experiments. First, because each nozzle is designed to generate a gas flow at a particular temperature for a particular density of the chosen carrier gas, it was not possible to measure TR-IRF traces for other than a single carrier gas density at each low temperature. Second, because of the large total gas flows and the low vapor pressure of CHT at room temperature, it was not possible to vary the parent/collider ratio in the gas flow. It was necessary to use the highest CHT concentration attainable using the "bubbler" system described in the Experimental section. Even then, the signal-to-noise ratio on the TR-IRF traces was not very high.

Three examples of kinetic decays of the IRF from toluene at low temperatures are displayed in Figure 2. These traces were analyzed according to eq (iv). Values of the parameters $k'$ and $b'$ for each low-temperature experiment are given in Table 3. They were converted to values of $k$ and $b$ using the rate coefficients $k_{LJ}$ shown in the fourth column of this table, which were calculated assuming that collisions occurred only with the carrier gas. As shown in Table 3, the mole fraction of CHT in

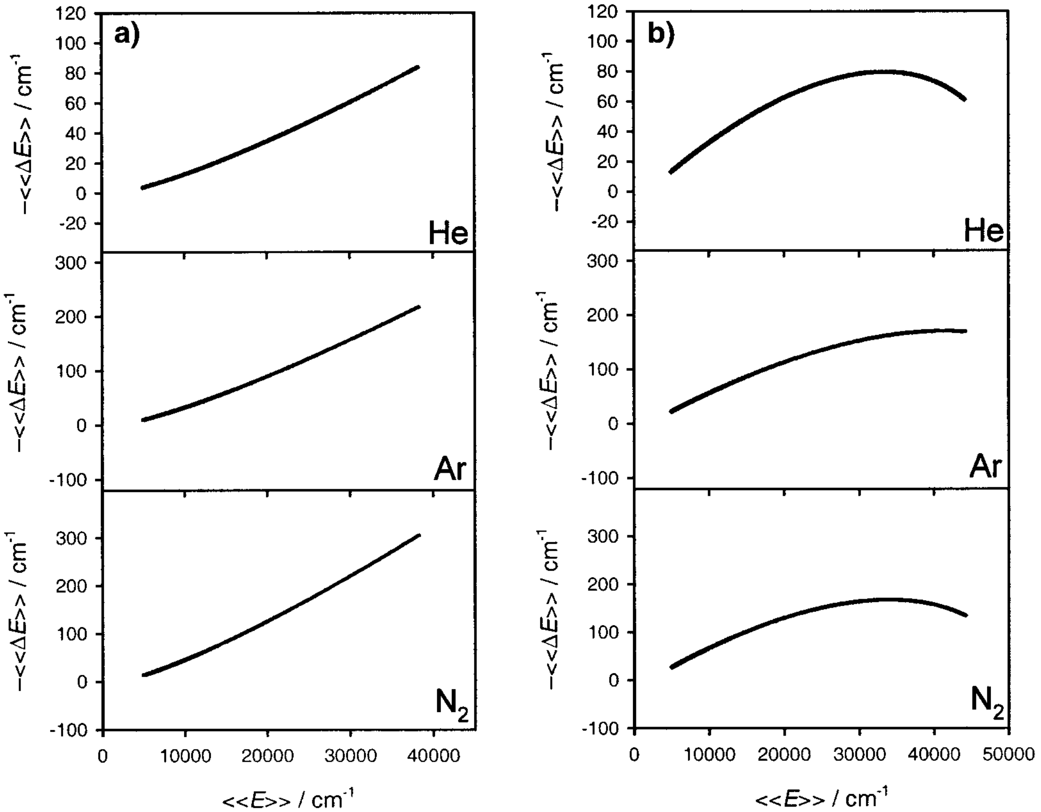

**Figure 1.** Plots of $-\langle\langle\Delta E\rangle\rangle$ versus $\langle\langle E\rangle\rangle$ for deactivation of excited toluene by He, Ar, and $N_2$ at room temperature: (a) with toluene excited directly by absorption of photons at 266 nm; and (b) with excited toluene formed via photoisomerization of CHT excited at 308 nm.

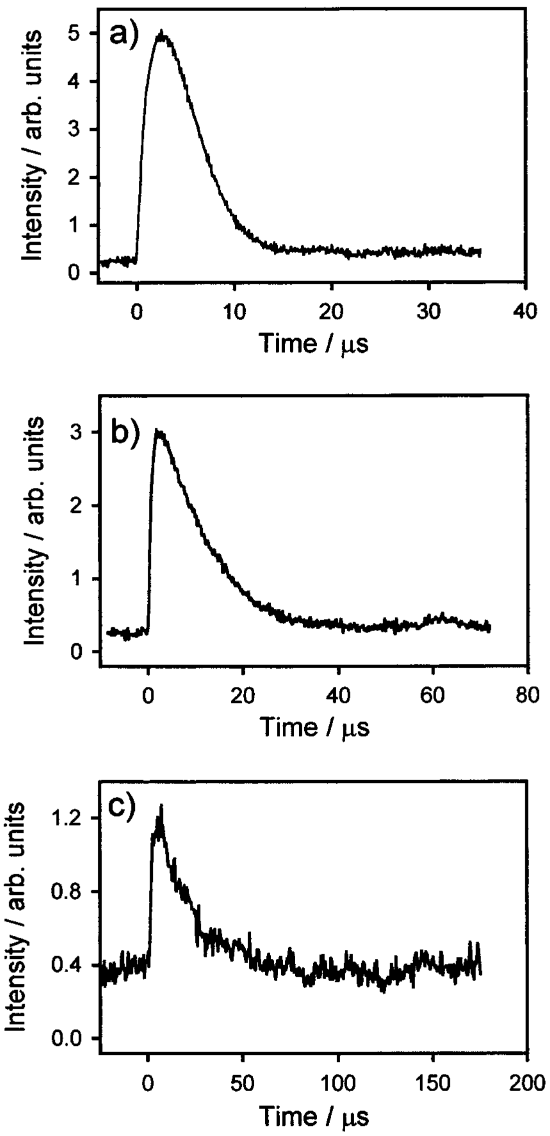

**Figure 2.** TR-IRF traces from excited toluene formed via photoisomerization of CHT excited at 248 nm in the CRESU apparatus: (a) in $5.83 \times 10^{16}$ molecule cm$^{-3}$ of $N_2$ at 207 K; (b) in $2.79 \times 10^{16}$ molecule cm$^{-3}$ of Ar at 112 K; and (c) in $2.08 \times 10^{16}$ molecule cm$^{-3}$ of He at 63 K.

the supersonic flow of gas was generally $< 2 \times 10^{-3}$, and always $\leq 4.1 \times 10^{-3}$.

Having obtained values of $k$ and $b$, the variation of $\langle\langle \Delta E\rangle\rangle$ with $\langle\langle E\rangle\rangle$ could be estimated as before. Curves of $\langle\langle \Delta E\rangle\rangle$ versus $\langle\langle E\rangle\rangle$ are displayed in Figures 3−5 for several different combinations of temperature and collider gas. Again the propagated errors in the values of $\langle\langle \Delta E\rangle\rangle$ are shown as lightly drawn curves. In Figure 6 the derived values of $-\langle\langle \Delta E\rangle\rangle$ for $\langle\langle E\rangle\rangle = 30\,000$ cm$^{-1}$ for toluene−He, toluene−Ar, and toluene−$N_2$ collisions are plotted against temperature.

## 5. Discussion

The values derived from our two sets of room-temperature experiments are compared in Table 2, both with one another and with the values derived by Toselli et al.[11] from experiments in which toluene was directly photoexcited at 248 nm. Given the different initial energies in these three sets of experiments and the approximate nature of the analysis, the agreement between these three sets of measurements is fairly good. In addition, our results can be compared with values of $\langle\langle E\rangle\rangle$ derived from the $P(E',E)$ curves for toluene−Ar and toluene−He collisions determined in the KCSI experiments of Luther and co-workers.[18] As they have pointed out, their measurements yield values of $\langle\langle E\rangle\rangle$ persistently higher than those obtained from TR-IRF and TR-UVA experiments, particularly for "weak" colliders such as He and Ar.

As in experiments performed by Barker's group, some of the curves of $-\langle\langle \Delta E\rangle\rangle$ against $\langle\langle E\rangle\rangle$ show "saturation"; that is, the values of $\langle\langle E\rangle\rangle$ become approximately constant or, in some cases, even start to decrease, at energies close to $E_{\text{initial}}$, the initial value of the excitation energy. This curious effect may be caused by a combination of two factors: the approximate nature of the fitting of the TR-IRF traces to the forms of eqs (iv) and (vi), coupled to the difficulty of observing genuine IRF signals at very short times because of the finite response time of the detector−amplifier combinations, used in both our experiments and those of Barker and co-workers. In general, by the time the fit is started, a few tens of collisions will have occurred, and the excited molecules will already have lost a significant amount of energy. Consequently, the values of $k'$ and $b'$ that are extracted from the experiments might differ significantly from those that would be derived if the whole curve from $t = 0$ onward could be observed. Such saturation effects are not observed in the TR-KCSI experiments where, if anything, the curves of $-\langle\langle \Delta E\rangle\rangle$ versus $\langle\langle E\rangle\rangle$ show a slight upward curvature at high $\langle\langle E\rangle\rangle$. The reason for the difference in $\langle\langle \Delta E\rangle\rangle$ values derived from TR-IRF and TR-KCSI experiments may be due to the fact that, in IRF experiments, the curves of IR intensity versus time are interpreted in terms of equations such as (iii) and (vii), which make no allowance for the spread of internal energies in an ensemble of relaxing molecules.

We recognize three possible sources of systematic error in the interpretation of our experimental data at low temperatures; in particular, the assumption that the kinetic decays of IRF are determined solely by collisional energy transfer from excited toluene molecules to the carrier gas, M. First, there is the possibility that, despite the small mole fraction of CHT, its role in deactivating the excited toluene molecules is not negligible. Second, there is the possibility that diffusion of excited toluene molecules out of the volume observed by the IR detector contributes to the fall in the intensity of emission. Finally, we have to consider the role played by the unimolecular decomposition of excited toluene molecules to benzyl radicals plus an H atom; i.e.,

$$C_6H_5CH_3^{\dagger} \rightarrow C_6H_5CH_2 + H \qquad \text{(ix)}$$

In considering these factors, it is as well to remember that the main purpose of the present experiments was to explore how the values of $\langle\langle \Delta E\rangle\rangle$ for M = $N_2$, Ar, and He vary with temperature down to values of temperature $< (\epsilon/k_B)$, rather than to obtain very precise values of $\langle\langle \Delta E\rangle\rangle$. Each of the three factors that might cause systematic errors should have similar effects at all temperatures.

Our measurements and those of others[16] show that, at room temperature, the ratio of $\langle\langle \Delta E\rangle\rangle_{\text{CHT}}$ to $\langle\langle \Delta E\rangle\rangle_{\text{M}}$ is approximately 6, 6, and 10 for M = $N_2$, Ar, and He, respectively. In our experiments below room temperature, the mole fraction of CHT is typically $2 \times 10^{-3}$, and in only one case (M = $N_2$ at 170 K) is it greater than $2.7 \times 10^{-3}$. These figures suggest that the contribution of CHT to the vibrational relaxation of excited toluene would have been less than 5%, in all of the low-temperature experiments, unless the ratio of $\langle\langle \Delta E\rangle\rangle_{\text{CHT}}$ to $\langle\langle \Delta E\rangle\rangle_{\text{M}}$ increases sharply as the temperature is lowered.

**TABLE 3: Experimental Conditions for the Fitting Parameters Obtained from Experiments in the CRESU Apparatus**

| $T$/K | M: [M] /$10^{16}$ cm$^{-3}$ | % CHT | $k_{LJ}$ /$10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $k$ /$(10^5$ s$)^{-1}$ | $b'$ /$(10^5$ s$)^{-2}$ | $k$ /$(10^{-2}$ Z$)^{-1}$ | $b$ /$(10^{-2}$ Z$)^{-2}$ |
|---|---|---|---|---|---|---|---|
| 207 | $N_2$: 5.83 | 0.17 | 5.0 | 1.25 ± 0.13 | 1.17 ± 0.09 | 0.43 ± 0.04 | 0.20 ± 0.01 |
| 170 | $N_2$: 0.57 | 0.41 | 4.9 | 0.424 ± 0.089 | 0 ± 0.013 | 1.52 ± 0.32 | 0 ± 0.2 |
| 168 | Ar: 9.01 | 0.27 | 4.3 | 2.28 ± 1.10 | 2.16 ± 1.12 | 0.59 ± 0.28 | 0.14 ± 0.07 |
| 149 | He: 1.44 | 0.14 | 6.1 | 0.380 ± 0.013 | 0 ± 0.002 | $0.43_5$ ± 0.015 | 0 ± 0.003 |
| 141 | Ar: 6.95 | 0.27 | 4.3 | 2.70 ± 0.44 | 0.42 ± 0.43 | 0.91 ± 0.04 | 0.05 ± 0.05 |
| 137 | Ar: 0.92 | 0.17 | 4.3 | 0.375 ± 0.25 | 0.089 ± 0.064 | 0.96 ± 0.63 | 0.58 ± 0.42 |
| 112 | Ar: 2.79 | 0.23 | 4.3 | 1.17 ± 0.043 | 0.136 ± 0.051 | 0.98 ± 0.04 | 0.096 ± 0.036 |
| 83 | $N_2$: 4.88 | 0.07 | 4.8 | 1.75 ± 0.38 | 1.77 ± 0.43 | 0.75 ± 0.16 | 0.33 ± 0.08 |
| 74 | $N_2$: 1.67 | 0.14 | 4.8 | 0.64 ± 0.23 | 0.11 ± 0.07 | 0.80 ± 0.28 | 0.17 ± 0.11 |
| 63 | He: 2.08 | 0.08 | 5.3 | 0.367 ± 0.068 | 0 ± 0.008 | 0.33 ± 0.06 | 0 ± 0.007 |
| 38 | He: 3.53 | 0.19 | 5.1 | 0.46 ± 0.09 | 0.012 ± 0.015 | 0.25 ± 0.05 | 0.004 ± 0.005 |

The units of $k'$ and $b'$ are chosen so that their values correspond to the values of $k't$ and $b't^2$ at a delay of 10 $\mu$s, i.e., $t = 10$ $\mu$s. The units of $k$ and $b$ are chosen so that their values correspond to the values of $kZ$ and $bZ^2$ after 100 collisions, i.e., $Z = 100$.

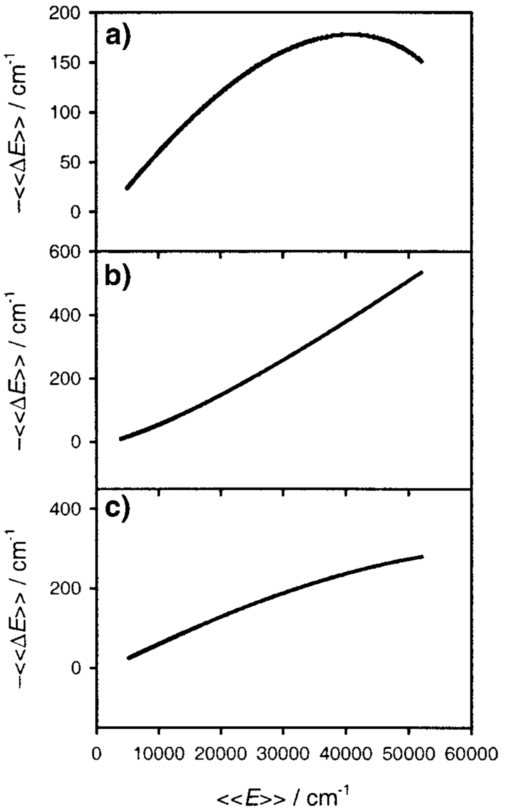

**Figure 3.** Plots of $-\langle\langle \Delta E\rangle\rangle$ versus $\langle\langle E\rangle\rangle$ for deactivation of excited toluene by $N_2$: (a) at 207 K; (b) at 170 K; and (c) at 74 K.

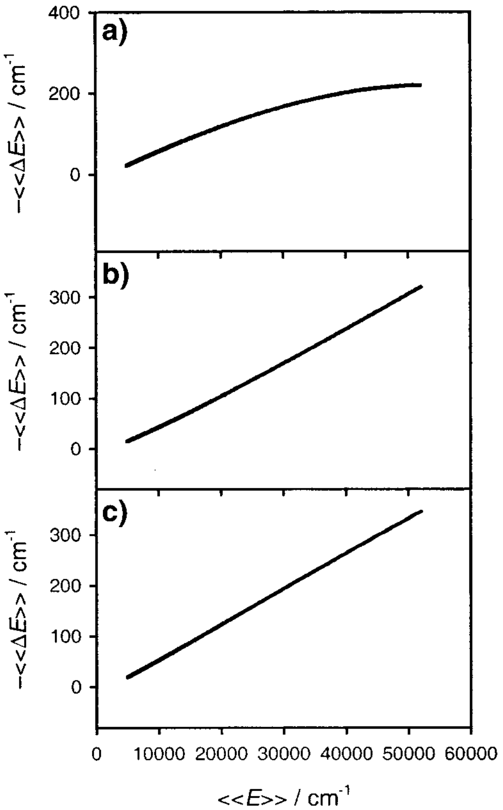

**Figure 4.** Plots of $-\langle\langle \Delta E\rangle\rangle$ versus $\langle\langle E\rangle\rangle$ for deactivation of excited toluene by Ar: (a) at 168 K; (b) at 141 K; and (c) at 112 K.

Any allowance for diffusive loss is difficult to estimate directly and impossible to measure in the present experiments. Using the standard formula for radial diffusion from a cylindrical volume, i.e., $\langle x^2\rangle^{1/2} = (4Dt)^{1/2}$, where $\langle x^2\rangle^{1/2}$ is the root-mean-square distance diffused in time $t$ and $D$ is the diffusion coefficient for the conditions of the system, we have estimated the values of $\langle x^2\rangle^{1/2}$ in 10 $\mu$s for the conditions of the experiments shown in Table 1. The largest value is for experiments in $N_2$ at 170 K, since the gas density is unusually low in the flow produced downstream from this nozzle. Even for this worst case, we find that $\langle x^2\rangle^{1/2}$ is only about 1 mm for $t = 10$ $\mu$s. As this distance is small relative to the dimensions of the volume illuminated by the excitation laser and observed by the IR detector, we conclude that diffusive loss does not make a significant contribution to the observed kinetic decays of IRF in our experiments. This conclusion is supported by consideration of earlier CRESU experiments[31] in which chemiluminescence from CH($A^2\Delta$) formed in the reaction between $C_2H$ and $O_2$ was used to determine the rates of a number of reactions of the $C_2H$ radicals. The experimental arrangement for formation of the radicals by excimer laser photolysis of $C_2H_2$ and observation of the chemiluminescence was similar to that used in the present experiments. The background, diffusion-determined, rate constant as [$O_2$] and [$C_2H_2$] both approached zero was between 1000 and 5000 s$^{-1}$, which is much less than the values of the first-order TR-IRF decay constants observed here.

The rate of unimolecular decomposition of CHT to benzyl plus H-atom has been studied by Troe and co-workers.[32,16b] At an excitation energy equivalent to 52 000 cm$^{-1}$, the energy dependent rate constant is equal to 1.5 $\mu$s$^{-1}$.[16b] The role played by this process depends on competition between it and collisional relaxation. The collision frequency for each experiment can be estimated by taking the product of the Lennard-Jones rate constant, $k_{LJ}$, and the density of M in that experiment. Again the experiment in $N_2$ at 170 K provides the worst case, because

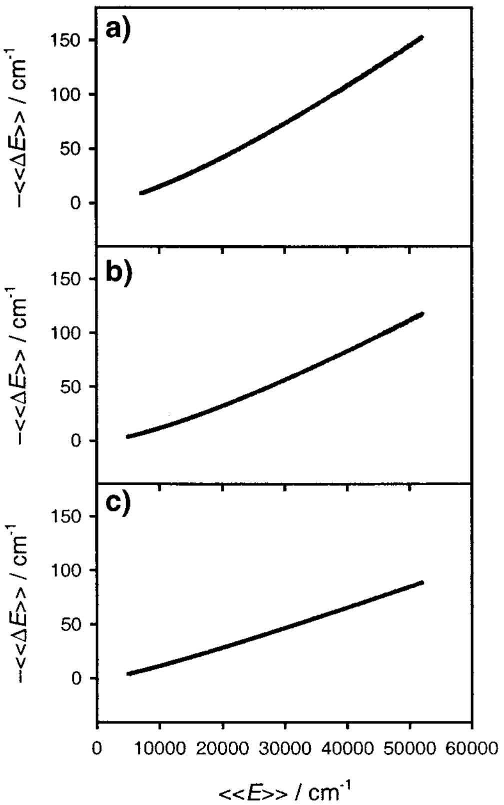

**Figure 5.** Plots of $-\langle\langle \Delta E \rangle\rangle$ versus $\langle\langle E \rangle\rangle$ for deactivation of excited toluene by He: (a) at 149 K; (b) at 63 K; and (c) at 38 K.

of the low density which lowers the collision frequency and the IRF decay time. In this case, $k_{LJ}$ [M] = 2.8 $\mu$s$^{-1}$ and clearly, when toluene molecules are first formed in this experiment, their unimolecular decomposition is competitive with collisional deactivation. However, three things should be borne in mind: (i) fitting of the IRF traces is only started several $\mu$s after the excimer laser is fired; (ii) the rate constants for decomposition depend strongly on the internal energy, so that after only a few collisions the decomposition rate will have fallen markedly from its value at zero time; and (iii) the experiment for which the above numbers have been calculated is much the worst case.

Finally, at the lowest temperatures of the experiments, one has to consider whether there is any dimerization, and subsequent condensation, of CHT. The rate of this process has not been measured, but Hamon et al.[33] have reported the rate of dimerization of benzene in helium at low temperatures (<100 K) and these results should provide a good model for dimerization of CHT. The measured rates were interpreted in terms of third-order rate constants which could be expressed as (1.0 $\times$ 10$^{-30}$) (T/298 K)$^{-2.7}$ cm$^6$ molecule$^{-2}$ s$^{-1}$. At 38 K and the density in our experiments at this temperature, this corresponds to a second-order rate constant for dimerization of ca. 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Given the concentration of CHT present in this experiment and the distance and speed of flow to the observation point, the extent of dimerization will be <5%. In other experiments at higher temperatures, dimerization should be entirely negligible.

Figure 6 shows plots of $\langle\langle \Delta E \rangle\rangle$ versus temperature for $\langle\langle E \rangle\rangle$ = 30 000 cm$^{-1}$ and M = N$_2$, Ar, and He. The values of $\langle\langle \Delta E \rangle\rangle$ for M = N$_2$ and Ar show insignificant changes with temperature, whereas for M = He $\langle\langle \Delta E \rangle\rangle$ decreases slightly as the temperature falls. One obvious difference between these two sets of systems is the greater well depth in the intermolecular potentials for toluene$-$N$_2$ ($\epsilon/k_B$ = 183 K) and toluene$-$Ar ($\epsilon/k_B$ = 216 K) compared with toluene$-$He ($\epsilon/k_B$ = 64 K).

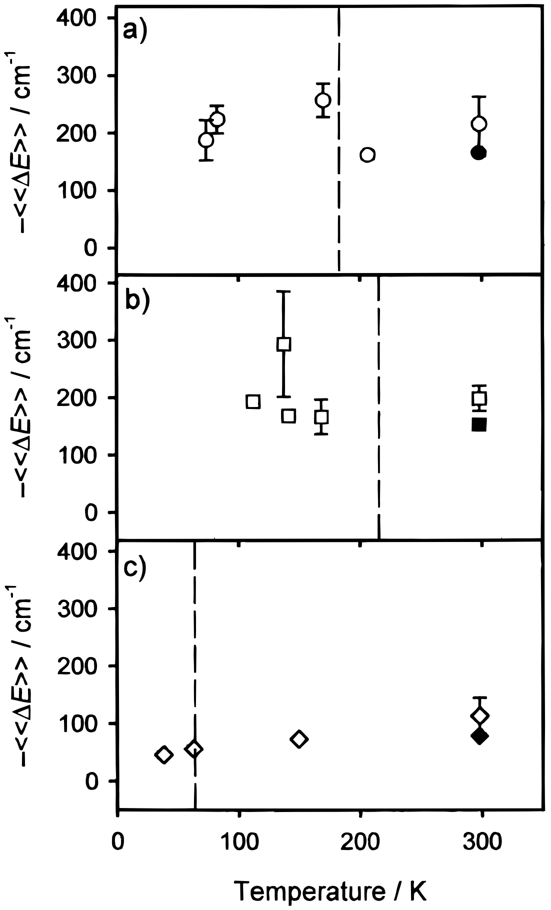

**Figure 6.** Plots of $-\langle\langle \Delta E \rangle\rangle$ at $\langle\langle E \rangle\rangle$ = 30 000 cm$^{-1}$ versus temperature for (a) N$_2$; (b) Ar; and (c) He. The open symbols are from experiments performed in the CRESU apparatus, the closed symbols from the experiments performed at room temperature in the simple cell. The dashed lines show the values of $\epsilon/k_B$ for the toluene$-$M collision pairs calculated by the usual combining rule, $\epsilon_{\text{toluene}-\text{M}} = (\epsilon_{\text{toluene}}\epsilon_{\text{M}})^{1/2}$.

A second difference between the systems toluene$-$N$_2$, toluene$-$Ar, and toluene$-$He is that, for a given collision energy, collisions with He are more impulsive. This makes it more likely, even at low temperatures, that energy transfer occurs via direct, single-encounter collisions of the kind invoked in SSH theory to bring about energy transfer. If so, then the kind of positive temperature dependence that we find would be expected. On the other hand, with slower-moving collision partners, it is possible that, at low temperatures, the collider may make multiple encounters with the vibrating peripheral atoms of the vibrationally excited molecule, in what have been called “chattering collisions”. Alternatively, the intermolecular attraction may accelerate the collision partners toward one another, thereby ensuring that the impulsiveness of collisions scarcely changes as the temperature is lowered.

Lenzer and Luther[18] have examined the effects of altering the well depth in Lennard-Jones interactions in their classical trajectory studies of collisions between highly excited benzene and noble gas atoms. By appropriate choice of ($\epsilon/k_B$), they were able to reproduce both the absolute magnitude of the values of $\langle\langle \Delta E \rangle\rangle$ and their dependence on $\langle\langle E \rangle\rangle$, but unfortunately they did not examine how the calculated results varied with collision energy or temperature. It is hoped that our results might stimulate further trajectory studies, thereby adding to our understanding of collisional relaxation of highly excited aromatic molecules.

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