# **Isomerization and Collisional Deactivation of Highly Vibrationally Excited Azulene** Molecules after UV Excitation at 248 and 193 nm

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Highly vibrationally excited azulene molecules in the electronic ground state were prepared by light absorption at 248 and 193 nm followed by internal conversion. Under collision-free conditions these molecules will isomerize to naphthalene. For azulene molecules excited with 193 nm ( $E = 52800 \text{ cm}^{-1}$ ), a specific rate constant of  $k(E) = (4.0 \pm 0.5) \times 10^5 \text{ s}^{-1}$  was determined. Isomerization of azulene excited with 248 nm ( $E = 41300 \text{ cm}^{-1}$ ) could not be observed under our experimental conditions. Collisional energy transfer from excited azulene to He, Ar, N<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, n-C<sub>8</sub>H<sub>18</sub>, and n-C<sub>8</sub>F<sub>18</sub> was also investigated by using time-resolved UV absorption spectroscopy. Absolute values of the average energy transferred per collision  $\langle \Delta E \rangle$  were in close agreement with results from previous studies. For large polyatomic colliders like n-C<sub>8</sub>H<sub>18</sub> and n-C<sub>8</sub>H<sub>18</sub>,  $\langle \Delta E \rangle$  values were found to be proportional to the average internal energy  $\langle E \rangle$  of the excited azulene molecule. However, for the small colliders He and Ar, only at energies up to about 15 000 cm<sup>-1</sup> does  $|\langle \Delta E \rangle|$  increase proportionally with  $\langle E \rangle$ , while at higher energies the energy dependence of  $|\langle \Delta E \rangle|$  becomes weaker. N<sub>2</sub> and C<sub>3</sub>H<sub>8</sub> represent intermediate cases.

# Introduction

Depending on the molecular complexity and the threshold energy, unimolecular reactions can have quite different energy dependences of specific rate constants k(E). For small molecules or large molecules with small barriers for reaction, k(E) can be covered by photochemical excitation simply by using wavelength variation (see, e.g., some examples in ref 1). This approach is not viable for large molecules where marked variations of k(E)occur only over very wide energy ranges. In this case, UV multiphoton excitation can be the method of choice, because with this technique large energy variations are possible unless a change of the photochemical excitation mechanism takes place. So far this concept was only applied to azulene isomerization to naphthalene,<sup>2</sup> but absolute measurements of specific rate constants were not possible. Instead k(E) was measured relative to collisional energy transfer and estimates of k(E) were made from thermal isomerization experiments.<sup>3</sup> For this reason, a direct measurement of k(E) for azulene isomerization appeared highly desirable.

The azulene molecule has photophysical properties which allow the preparation of energy-selected vibrationally highly excited molecules in the electronic ground state over relatively wide ranges of energy. The electronic absorption spectrum extends from the red spectral region through the visible to the UV region.<sup>24,5</sup> The  $S_0 \rightarrow S_1$  transition is located near 15000 cm<sup>-1</sup>, the  $S_0 \rightarrow S_2$ transition near 29 000 cm<sup>-1</sup>, the  $S_0 \rightarrow S_3$  transition near 34 000 cm<sup>-1</sup>, the  $S_0 \rightarrow S_4$  transition near 35 000 cm<sup>-1</sup>, and the  $S_0 \rightarrow S_5$  transition near 42 000 cm<sup>-1.6.7</sup> Like excitation into the  $S_1$  state, excitation into the  $S_2$  state is followed by a rapid internal conversion to the electronic ground state with a quantum yield of 0.96.<sup>8</sup> From excitation into higher states like  $S_3$  or  $S_4$ , almost identical fluorescence spectra have been observed as from molecules in the  $S_2$  state. This is due to very fast internal conversion

from  $S_3$  and  $S_4$  to  $S_2^9$  which is then followed by the internal conversion to S<sub>0</sub>. Therefore, one can assume that azulene molecules, which are excited with light in the region between 700 and 190 nm (corresponding to excitation energies between about 14000 and 53 000 cm<sup>-1</sup>), will end up as vibrationally excited molecules in the electronic ground state with a quantum yield close to unity. The construction of specific rate constants for azulene isomerization, based on measurements of the thermal isomerization,<sup>2,3</sup> suggested that direct k(E) measurements would only be possible at the short-wavelength end of the absorption spectrum. It was the goal of the present work to investigate this possibility.

The possibility of preparing vibrationally highly excited electronic ground state molecules can be exploited for studies of collisional energy transfer. Azulene here has served as a prototype system using various initial excitation energies. In order to measure average energies transferred per collision, the energy content of the excited molecules has to be monitored during the stepwise deactivation in collisions with heat bath molecules. The methods most widely used are time-resolved UV absorption spectroscopy  $(UVA)^{10-12}$  and time-resolved infrared fluorescence (IRF).<sup>13</sup> Both methods have also been employed to study the collisional deactivation of azulene by various inert bath gases [UVA,<sup>5,14,15</sup> IRF,<sup>16-20</sup>). Good agreement has been found between absolute values of  $\langle \Delta E \rangle$  obtained by the two different methods. However, some differences remained in the experimentally determined energy dependence of  $(\Delta E)$  values. It has been proposed<sup>21</sup> that an investigation of collisional deactivation starting at excitation energies around 50000 cm<sup>-1</sup> should clarify the uncertainties in the energy dependence of  $\langle \Delta E \rangle$ . Most previous investigations studied the collisional deactivation of azulene for

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initial excitation energies below 30000 cm<sup>-1</sup>. Higher vibrationally excited azulene molecules, prepared via 248-nm absorption, have so far only been used to monitor the collisional energy gain in the lowest vibrational levels of  $CO_2$ .<sup>22</sup> In the present work the collisional deactivation of azulene is studied after excitation at 248 nm ( $\langle E \rangle = 41300$  cm<sup>-1</sup>) and 193 nm ( $\langle E \rangle = 52790$  cm<sup>-1</sup>). The initial excitation energy of azulene here is given by the sum of the photon energy and the initial thermal energy of 979 cm<sup>-1</sup> at 300 K.

#### **Experimental Technique**

Our experimental arrangement has been described in detail elsewhere<sup>5,11</sup> and will be summarized only briefly in the following. Analysis light from a continuous Xe-Hg arc lamp (Ushio UXM-200H, 200 W) passed through a cylindrical glass reaction cell (length 50 cm, diameter 2.3 cm). The transmitted light was dispersed in a quartz prism double monochromator (Zeiss MM12) and recorded with a photomultiplier (RCA 1P28A) connected to a transient digitizer (LeCroy TR 8837F). Excitation light was obtained from an excimer laser (Lambda Physik EMG 150) operated with  $Ar/F_2/He$  or  $Kr/F_2/He$  mixtures to produce laser light at 193 or 248 nm. The excitation laser beam was conducted through the reaction cell beam-in-beam with the analysis light. The laser pulses had a duration of about 20 ns and a fluence of between 0.5 and 1.5 mJ/cm<sup>2</sup> at 193 nm and 0.5 and 1 mJ/cm<sup>2</sup> at 248 nm. The fluences were either measured directly with a calibrated GenTec ED-200 Joulemeter or determined by actinometry (see ref 23). Ethylbenzene and cycloheptatriene were used as actinometer substances for excitation at 193<sup>24</sup> and 248 nm,<sup>25</sup> respectively. Under these fluence conditions at maximum 10% of the azulene molecules were excited directly behind the entrance window. Therefore, perturbations due to multiphoton excitation were negligible.

Azulene (Sigma or Aldrich, >99%) was purified by several sublimation-resublimation cycles. The bath gases He (99.996%), Ar (99.998%), N<sub>2</sub> (99.996%), and C<sub>3</sub>H<sub>8</sub> (99.95%) were all from Messer Griesheim and used without further purification. n-C<sub>8</sub>H<sub>18</sub> (Fluka, >99.8%) and n-C<sub>8</sub>F<sub>18</sub> (Fluka, >99.8%) were carefully degassed by pump-freeze cycles.

Isomerization of Azulene to Naphthalene. After excitation at 193 nm, absorption-time profiles were monitored at wavelengths between 280 and 300 nm. Excitation at 248 nm did not lead to reaction under our experimental conditions. The reaction here is too slow to compete with collisional deactivation or diffusion out of the observation volume. All measurements were performed in a flow system to prevent accumulation of naphthalene. Azulene was preheated to 80 °C in an oven and a constant flow from the oven into the reaction cell was realized by using a MKS 1150A flow controller. Experiments with pure azulene at 193 nm were carried out at total pressures between 2.5 and 7  $\mu$ bar. In order to prevent perturbations due to the flight of excited molecules out of the observation volume, here the diameter of the laser beam (1.2 cm) was chosen twice the diameter of the analysis light beam. Competition between isomerization and collisional deactivation by nitrogen has also been investigated in experiments at 193 nm, see below. A Tylan FC-260 (maximal flow 20 sccm) flow controller was employed to ensure a constant nitrogen flow which was mixed with the azulene flow. Nitrogen pressures between 0.1 and 0.5 mbar were chosen. Typically, several hundred laser shots were averaged.

In separate experiments azulene under its own vapor pressure at room temperature was irradiated by several hundred laser pulses at 193 nm. By use of UV-absorption spectroscopy, only naphthalene was detected as a photoproduct.



Figure 1. Absorption-time profile of collision-free unimolecular isomerization of azulene to naphthalene in the electronic ground state (laser excitation at 193 nm, analysis wavelength 290 nm,  $P(azulene) = 5 \mu bar$ ; superposition of absorption signals from disappearing azulene and appearing naphthalene).



Figure 2. As in Figure 1, but in the presence of small concentrations of the bath  $N_2$  (*P*(azulene) = 10  $\mu$ bar, *P*( $N_2$ ) = 0.17 mbar).

Collisional Energy Transfer. Vibrationally highly excited molecules for collisional energy transfer studies were produced by excitation at 193 or 248 nm. Absorption-time profiles were monitored at 290 nm. All measurements were made near 298 K. The azulene concentration in the reaction cell was very low because of its low vapor pressure (12.1  $\mu$ bar at 25 °C). In these experiments, pressures of collider gases were chosen high enough that the quantum yield for isomerization was negligible. For each collision partner, experiments were carried out at different bath gas pressures to ensure that only collisional deactivation of the vibrationally excited azulene molecules was observed. For example, measurements with argon as a deactivating collider were performed with p(Ar) = 3 mbar and p(Ar) = 6 mbar. Under these conditions deactivation of excited azulene molecules by cold azulene molecules is negligible. Typically, around 500 shots were averaged.

## Results

Isomerization. Figure 1 shows an absorption-time profile monitored at 290 nm after excitation of pure azulene vapor (p = 5  $\mu$ bar) at 193 nm. At 290 nm the absorption coefficient of "hot" azulene is much larger than the absorption coefficient of "cold" azulene ( $\epsilon(\langle E \rangle = 30\,000 \text{ cm}^{-1})/\epsilon(\langle E \rangle = 979 \text{ cm}^{-1}) =$  $6.3.^{14}$ ). Obviously, the fast increase in absorption is due to the formation of vibrationally excited azulene molecules during the laser pulse. The decrease of absorption with increasing time is caused by the disappearance of hot azulene and the appearance of hot naphthalene molecules in the isomerization reaction. The final absorption level must exclusively stem from the absorption of the produced hot naphthalene. Its internal energy has increased by the reaction enthalpy of  $\Delta H^{\circ}_{0} = 11\,000 \text{ cm}^{-1}$  to  $\langle E \rangle = 63\,790$ cm<sup>-1</sup> compared to the initial energy of the azulene molecules of 52 790 cm<sup>-1</sup>. Apparently, the absorption coefficient of these hot naphthalene molecules is about one-half of the absorption coefficient of hot azulene. A variation of the azulene pressure between 2.5 and 7  $\mu$ bar did not influence the observed reaction kinetics. Therefore, one can safely assume that no deactivating collisions perturbed the observed reaction. The evaluation of the absorp-

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Figure 3. Apparent specific rate constant k of azulene isomerization to naphthalene in the presence of the bath gas  $N_2$  (laser excitation at 193 nm).



**Figure 4.** Absorption-time profile of collisional deactivation of vibrationally highly excited azulene by argon (laser excitation at 193 nm, analysis wavelength 290 nm, P(Ar) = 4.1 mbar).

tion-time profile yielded a specific rate constant, for azulene isomerization to naphthalene, of  $k(E) = (4.0 \pm 0.5) \times 10^5 \text{ s}^{-1}$  with  $E = 52\,790 \text{ cm}^{-1}$ .

Figure 2 shows an absorption-time profile monitored at 290 nm after 193-nm excitation of azulene in a mixture with 0.17 mbar of nitrogen. Under these conditions the process is governed by a competition between isomerization and collisional energy transfer. The absorption decay directly after excitation is dominated by isomerization. For about 2  $\mu$ s the absorption then remains almost constant. The reaction has terminated and the absorption coefficient of the azulene-naphthalene mixture here is almost independent of the excitation energy. Therefore, the absorption does not decay during the initial collisional deactivation. At later times the absorption decays because of decreasing absorption coefficients during the loss of internal energy. In Figure 2 the isomerization yield is smaller than under collision-free conditions (see Figure 1) because a fraction of the initially vibrationally highly excited azulene molecules is stabilized by collisional deactivation.

In Figure 3 the apparent increase of the effective first-order rate constant for the isomerization is shown as a function of the  $N_2$  bath gas pressure. A Stern-Volmer plot of the apparent isomerization rate constant<sup>26</sup>

$$k_{\rm app}(\langle E_{\rm ac} \rangle) \approx k(\langle E_{\rm ac} \rangle) \{1 + y_{\rm c} Z[M] / k(\langle E_{\rm ac} \rangle)\}$$
(1)

with the data of Figure 3 leads to a collision efficiency for the stabilization of  $y_c = 0.19 \pm 0.06$ . The corresponding collision efficiency can also be approximated by<sup>26</sup>

$$\frac{y_{\rm c}}{1-y_{\rm c}^2} = \frac{\langle \Delta E \rangle s}{\langle E_{\rm ac} \rangle - E_0} \tag{2}$$

With s = 9.5,  $E_0 = 22000$  cm<sup>-1</sup> (from ref 3),  $\langle E_{ac} \rangle = 52790$  cm<sup>-1</sup>, and  $\langle \Delta E \rangle (E) = 440$  cm<sup>-1</sup> (see below), one obtains  $y_c = 0.13$  which agrees within the experimental uncertainty with the value determined from Figure 3 and reveals the consistency of this measurements and with the energy-transfer experiments described below.



Figure 5. As in Figure 4, but time axis calibrated in number  $Z_{LJ}[M]t$  of Lennard-Jones collisions (curve 1 from Figure 5, curve 2 with laser excitation at 248 nm).

Collisional Energy Transfer. Figure 4 shows a typical absorption-time profile for collisional deactivation of vibrationally excited azulene. Again a sharp absorption increase is observed due to the formation of vibrationally highly excited molecules in the electronic ground state during the laser pulse. As time evolves, excited azulene molecules are deactivated by collisions with the surrounding bath gas molecules. The isomerization is completely quenched and the absorption stays constant until further deactivation leads to the decrease of the absorption coefficient which is reflected by the decay in the absorption coefficient at 290 nm of azulene as a function of its energy content (see Figure 6 in ref 14), absorption-time profiles can be converted into energy-loss profiles which were evaluated by using the simple expression<sup>27</sup>

$$d\langle E \rangle / dt = ZP \langle \Delta E \rangle \tag{3}$$

Here Z denotes the collision frequency, P the pressure, and  $\langle \Delta E \rangle$  the average energy transferred per collision. It is known that this simple equation is valid only for inefficient collisions when the distribution of excited states is still far from the final thermal equilibrium. This is clearly fulfilled under our conditions. The analysis can only provide the product  $Z\langle\Delta E\rangle$  via eq 3. For illustrative purposes it is practical to separate this product into a specified collision frequency and to present  $\langle\Delta E\rangle$  values relative to this collision frequency. Here, Lennard-Jones collision frequencies from ref 15 were employed to derive  $\langle\Delta E\rangle$  values.

The evaluation of absorption-time profiles is rendered difficult at high excitation energies. The calibration curve  $\epsilon(\langle E \rangle)$  levels off for energies above 30 000 cm<sup>-1.14</sup> At the highest excitation energies, the energy independence of the absorption coefficient can be recognized in the initial part of absorption-time profile in Figure 4 where the absorption stays almost constant after excitation at 193 nm. At these energies, an absorption-time profile cannot be uniquely transformed into an energy-loss profile. This problem exists for all excitation wavelengths smaller than 300 nm.<sup>14</sup> On the other hand, for larger wavelengths the absorption difference between hot and cold azulene molecules becomes too small to allow for precise measurements. A way out of this dilemma is provided by the comparison of absorption-time profiles recorded after excitation at 193 and 248 nm.

As long as the simple evaluation via eq 3 is valid, the absorption-time profiles starting with an excitation energy of 52 790 cm<sup>-1</sup> (193 nm) after a while should coincide with the profiles starting at energies of 41 300 cm<sup>-1</sup> (248 nm). In Figure 5 we have scaled the two absorption-time profiles after excitation at 193 and 248 nm and obtained a perfect match for energies below 41 300 cm<sup>-1</sup>. From the time difference between the two absorption steps one derives the number of collisions with the heat bath required for relaxation from 52 790 to 41 300 cm<sup>-1</sup>. On this basis average  $\langle \Delta E \rangle$  values ( $\langle \Delta E \rangle_{av}$ ) for deactivation over this energy interval can be calculated. Although only an average value of  $\langle \Delta E \rangle$  is obtained, it should be noticed one has the advantage that this result is independent of the quality  $\epsilon(\langle E \rangle)$  calibration curve. Due to uncertainties in the scaling procedure, the accuracy of the  $\langle \Delta E \rangle_{av}$  values is estimated to be about 20%.  $\langle \Delta E \rangle_{av}$  values are derived

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**Figure 6.** Average energies  $\langle \Delta E \rangle$  as a function of excitation energy  $\langle E \rangle$ for collisions of vibrationally highly excited azulene molecules with He (1, this work; 2, ref 15; 3, ref 5).



Figure 7. As in Figure 6, but with bath gas Ar.



Figure 8. As in Figure 6, but with bath gas  $N_2$ .



Figure 9. As in Figure 6, but with bath gas  $C_3H_8$ .

in this way for excitation energies between 41 300 and 52 790 cm<sup>-1</sup>. Energy-dependent  $\langle \Delta E \rangle$  values, which are not averaged over a larger energy range, are obtained for energies below 41 300 cm<sup>-1</sup> by using the calibration curve  $\epsilon(\langle E \rangle)$  of ref 14. The results for various bath gases are shown in Figures 6-11. From various reconstructions of the absorption-time profiles the accuracy of the derived  $\langle \Delta E \rangle$  values is estimated to be about 30% at 50 000 cm<sup>-1</sup> and 20% at 30 000 cm<sup>-1</sup>.

## Discussion

Isomerization. The reconstruction of specific rate constants k(E) from thermal unimolecular reaction rates is subject to certain uncertainties. First of all, one has to be sure that there no falloff corrections of the measured high-pressure rate constants  $k_{\infty}$  are necessary. Furthermore, the reconstruction of a two-parameter expression for k(E) from the two-parameter expression  $k_{\infty}$ (preexponential factor  $A_{\infty}$  and activation energy  $E_{a\infty}$ ) is not unique and is dependent on the accuracy of  $E_{a\infty}$  determination. Our





Figure 10. As in Figure 6, but with bath gas  $n-C_8H_{18}$ .



Figure 11. As in Figure 6, but with bath gas  $n-C_8F_{18}$ .



Figure 12. Specific rate constants k(E) for isomerization of azulene to naphthalene in the electronic ground state (O, absolute results from this work;  $\blacklozenge$ , relative results from UV two-photon excitation in ref 2;  $\blacklozenge$ , indirect results from molecular beam measurements in ref 31).

earlier experience with a similar problem in the thermally and photochemically induced isomerization of cycloheptatriene<sup>28-30</sup> here may serve as an example. The k(E) values derived from the RRKM deconvolution of the thermal  $k_{\infty}$  values<sup>28</sup> as well as from Stern-Volmer plots of photoisomerization quantum yields<sup>29</sup> in this case finally had to be modified by a factor of 3, after a direct k(E)measurement became available from laser excitation experiments.<sup>30</sup> A similar observation was made here. The experimentally obtained specific rate constant  $k(E) = (4.0 \pm 0.5) \times 10^5 \text{ s}^{-1}$  at  $\langle E \rangle = 52790$ cm<sup>-1</sup> is about a factor of 3 smaller than the value derived from the RRKM deconvolution (see Figure 12). Taking into account that the excitation energy is well in the range where the highest accuracy of the RRKM deconvolution is expected, the agreement between experimental and predicted k(E) value is not very good but the result corresponds to our experience with the cycloheptatriene system. Two more experimental k(E) values from photoexcitation experiments are included in Figure 12. One of these measurements came from UV two-photon excitation experiments with quantum yield measurements<sup>2</sup> in which, at various laser fluences, k(E) was determined relative to collisional energy transfer. In this case, an absolute calibration of k(E) or  $\langle \Delta E \rangle$ would be required for a unique analysis. The other measurement

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TABLE I: Comparison of Average Energies  $\langle \Delta E \rangle$  (in cm<sup>-1</sup>) Transferred per Collision between Excited Azulene and Various Bath Gases<sup>a</sup>

excitn wavelength/cm	$\langle E \rangle = 25020 \text{ cm}^{-1}$			$\langle E \rangle = 14920 \text{ cm}^{-1}$		
	193/248	337	337	193/248	590	600
detection	UVA	UVA	IRF	UVA	UVA	IRF
reference	this work	12	20	this work	3	20
Не	95	79	97	67	75	20
Ar	205	205	235	155	160	134
N <sub>2</sub>	245	195	330	160	175	135
2C,H,	790	770		520	600	
n-C.H.	1720	1170		1080	870	
n-C <sub>8</sub> F <sub>18</sub>	1580	1250		1035	1050	

 $^{a}T = 298$  K, all values calculated relative to the Lennard-Jones collision frequencies from ref 15, UVA = detection by ultraviolet absorption, IRF = detection by infrared fluorescence.

stems from molecular beam experiments in which<sup>31</sup> relatively large uncertainties about k(E) and E were still present. In spite of these problems, the general agreement between the k(E) measurements at quite different energies and the k(E) curve obtained from RRKM deconvolution of thermal isomerization experiments appears most satisfactory. It is remarkable in the sense that it encompasses changes of directly measured k(E) over 5 orders of magnitude at energy variations from about 30 000 to 70 000 cm<sup>-1</sup>.

Collisional Energy Transfer. In the investigated energy range,  $\langle \Delta E \rangle$  increases with increasing energy. However, the exact energy dependence cannot be inferred from the present experiments alone. For some collision partners, there appears to be a transition to a weaker energy dependence of  $\langle \Delta E \rangle$  with increasing  $\langle E \rangle$ , since most of the  $\langle \Delta E \rangle$  curves do not simply extrapolate to  $\langle \Delta E \rangle =$ 0 at  $\langle E \rangle = \langle E \rangle_{\text{th}}$ . There appears to be a stronger increase of  $\langle \Delta E \rangle$ with energy at lower excitation energies than at higher energies which is in agreement with the experiments of ref 5 starting at an initial excitation energy of 18 000 cm<sup>-1</sup> (see below).

The most reliable  $\langle \Delta E \rangle$  values are obtained close to the initial excitation energy. At greater deactivation times the energy distribution of the excited molecules may have broadened so much that an increasing part of the molecules may have reached thermal equilibrium while collisional deactivation of the other molecules still proceeds. Under such conditions also, the  $\epsilon(\langle E \rangle)$  calibration curve has to be known with great precision and a complete solution of the master equation is required. In addition, the last part of the absorption-time profile may be perturbed by pressure waves or, at low bath gas pressures, by diffusion of the excited molecules out of the observation volume. A comparison of absolute  $\langle \Delta E \rangle$ values obtained close to different initial excitation energies, therefore, should lead to the safest information of the energy dependence of  $\langle \Delta E \rangle$ . One should note that the present results, for deactivation from 53 000 to 41 000 cm<sup>-1</sup> are particularly reliable, since they do not depend on a calibration curve of the detection method.

Figures 6-11 and Table I compare the results from different initial excitation energies. There is good internal consistency in the absolute  $\langle \Delta E \rangle$  values. However, the experiments starting with an initial excitation energy of 30 600 cm<sup>-1 15</sup> suggested that  $\langle \Delta E \rangle$  becomes nearly independent of  $\langle E \rangle$  for excitation energies above about 20 000 cm<sup>-1</sup>. This behavior was derived from the curvature of the deduced energy-time profile. However, this leveling off of the energy dependence of  $\langle \Delta E \rangle$  cannot be confirmed by the present study. Absolute  $\langle \Delta E \rangle$  values for energies above 40 000 cm<sup>-1</sup> are clearly above the  $\langle \Delta E \rangle$  values deduced in ref 15.





Figure 13. As in Figure 6, but with bath gas Ar. Comparison of UV absorption (full lines) and IR fluorescence (dashed lines) results (1, this work; 2, ref 5; 3, ref 20).

Nevertheless, a comparison with the results from ref 3 for excitation energies below 10000 cm<sup>-1</sup> suggests that, for all colliders except *n*-octane and *n*-perfluorooctane, the energy dependence of  $\langle \Delta E \rangle$  is stronger at low excitation energies than at high excitation energies.

Within the experimental uncertainty, there is good agreement between the absolute  $\langle \Delta E \rangle$  values obtained from IRF and UVA for almost all colliders. For a comparison, results from ref 20 are given in Table I. In Figure 13 the energy dependences of  $\langle \Delta E \rangle$ are compared for argon as collider gas. The IRF results indicated an almost linear relationship between  $\langle \Delta E \rangle$  and  $\langle E \rangle$  at least up to energies around 30 000 cm<sup>-1</sup>, while the present UVA results suggest a weaker energy dependence of  $\langle \Delta E \rangle$ . An extrapolation toward  $\langle \Delta E \rangle$  values at higher excitation energies using the energy dependence from the IRF measurements would have led to  $\langle \Delta E \rangle$  $\approx -420$  cm<sup>-1</sup> at 40000 cm<sup>-1</sup> and  $\langle \Delta E \rangle \approx -520$  cm<sup>-1</sup> at 50000 cm<sup>-1</sup>. Our experiment from excitation at 193 and 248 nm results in a mean  $\langle \Delta E \rangle$  value of  $\langle \Delta E \rangle_{av} = -(300 \pm 60)$  cm<sup>-1</sup> between  $\langle E \rangle$ = 52 790 and 41 300 cm<sup>-1</sup> (see Figure 5).

For most bath gases the observation from ref 21 was confirmed that, for large polyatomic molecules, the energy dependence of  $\langle \Delta E \rangle$  decreases with increasing excitation energy. However, compared with other large polyatomic molecules like toluene<sup>11</sup> and cycloheptatrienes<sup>32</sup> the energy dependence at high excitation energies seems to be somewhat stronger in the azulene system. Further experiments investigating collisional energy transfer of vibrationally excited azulene by the more detailed method of kinetic controlled selective ionization (KCSI) are underway.<sup>33</sup>

So far, theoretical models only semiquantitatively reproduce the experimental results. For the deactivation of azulene by rare gases, trajectory calculations by Gilbert and Lim<sup>34,35</sup> have been made. However, random walk analysis of the energy flow in a single collision event, which was applied in this work, cannot completely reproduce the observed features of the energy-transfer parameters. The agreement between the  $\langle \Delta E \rangle$  values from new theoretical calculations<sup>35</sup> and from experiment is adequate for heavy rare gases but terrible for the light gases, and the predicted energy dependence of  $\langle \Delta E \rangle$  for the heavy rare gases between  $\langle E \rangle$ = 15000 cm<sup>-1</sup> and  $\langle E \rangle$  = 30000 cm<sup>-1</sup> appears to be much too weak.

Acknowledgment. Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB 93) "Photochemie mit Lasern" is gratefully acknowledged.

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