

Infrared multiphoton excitation of CF₃I. II. Collisional energy transfer of vibrationally highly excited CF₃I

B. Abel, B. Herzog, H. Hippler, and J. Troe

Citation: *J. Chem. Phys.* **91**, 900 (1989); doi: 10.1063/1.457141

View online: <http://dx.doi.org/10.1063/1.457141>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v91/i2>

Published by the [American Institute of Physics](#).

Additional information on *J. Chem. Phys.*

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



**ACCELERATE COMPUTATIONAL CHEMISTRY BY 5X.
TRY IT ON A FREE, REMOTELY-HOSTED CLUSTER.**

[LEARN MORE](#)

Infrared multiphoton excitation of CF₃I. II. Collisional energy transfer of vibrationally highly excited CF₃I

B. Abel, B. Herzog, H. Hippler, and J. Troe

Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße 6, D-3400 Göttingen, West Germany

(Received 1 December 1988; accepted 20 March 1989)

Energy transfer of vibrationally highly excited CF₃I molecules ($E \approx 18\,000\text{ cm}^{-1}$) in collisions with argon, propane, and octane was studied using hot UV absorption spectroscopy of CF₃I. The preparation of the excited CF₃I was achieved by IR multiphoton absorption which, under the conditions applied, produces a narrow initial energy distribution of CF₃I near to the dissociation energy. The average energies $\langle \Delta E \rangle$ transferred per collision were found to be proportional to E for the bath gases propane and octane; they showed a stronger increase with energy at low excitation energies in the bath gas argon. The energy dependence of $\langle \Delta E \rangle$, therefore, is not only governed by the properties of the excited molecule (e.g., its density of states) but also by features of the collision partner (e.g., the magnitude of $\langle \Delta E \rangle$). At energies near to the dissociation energy for all colliders, $\langle \Delta E \rangle$ was found to approach values similar to those obtained from single UV photon excitation experiments with highly excited triatomic and large polyatomic molecules.

I. INTRODUCTION

Collisional energy transfer of vibrationally highly excited molecules continues to be a central problem in gas phase chemical kinetics. Over the last decade "direct" laser excitation experiments have considerably extended the information derived earlier from more "indirect" experiments using chemical, thermal, or photochemical activation techniques.^{1,2} A recent review of the state of the art³ reveals areas which have not been covered by the now often applied laser induced internal conversion technique.⁴⁻⁸ Single UV (or visible) photon excitation followed by internal conversion to the vibrationally highly excited electronic state requires the presence of an excited electronic state mixing efficiently with the ground state. In this way, energy transfer in highly excited CS₂ and SO₂⁷ as well as in excited large polyatomic molecules like azulene, toluene, cycloheptatriene, hexafluorobenzene etc. became accessible.^{4-6,8} While the average energies $\langle \Delta E \rangle$ transferred per collision of these molecules with various bath gases are comparable at high-excitation energies, the energy dependences of $\langle \Delta E \rangle$ at lower energies appear to be quite different. $\langle \Delta E \rangle \propto E^2$ was found⁷ for CS₂ and SO₂ whereas $\langle \Delta E \rangle \propto E$ was observed for larger polyatomic molecules^{5,6} as long as the energy was not too large. At energies above about $20\,000\text{ cm}^{-1}$ a transition to a nearly energy independent $\langle \Delta E \rangle$ was determined for large polyatomic molecules.^{4,6,10} On the other hand, at low energies a transition between $\langle \Delta E \rangle \propto E^2$ and $\langle \Delta E \rangle \propto E$ in the form $\langle \Delta E \rangle \propto E^{3/2}$ was measured¹¹ for a molecule of intermediate size like SF₆ after CO₂ laser excitation.^{11,12}

The experiments on SF₆ using CO₂ laser excitation have started to bridge the gap between the energy transfer of excited triatomic and polyatomic molecules. An interpretation of the changing energy dependence of $\langle \Delta E \rangle$ between a proportionality to E or E^2 was suggested in Ref. 3: Classical trajectory calculations (see review in Ref. 3) in general have led to

a prediction of $\langle \Delta E \rangle \propto E$ whereas an additional energy dependence in Ref. 3 was related to the sparsity of the vibrational quasicontinuum. In order to obtain a clearer picture, more experimental information for molecules of intermediate size is required. In particular, it appears important to investigate whether different energy dependences of $\langle \Delta E \rangle$, being between $\langle \Delta E \rangle \propto E^2$ and $\langle \Delta E \rangle \propto E$, can be observed for different collision partners of the same excited molecule. This could provide a closer relation between the properties of $\langle \Delta E \rangle$ and the sparsity of the vibrational quasicontinuum. Unfortunately, there are not too many molecules of intermediate size for which the single photon excitation via internal conversion could be employed conveniently. However, IR multiphoton excitation provides the access to a large class of suitable candidates for energy transfer studies of the described kind. The only disadvantage of this approach lies in the difficulty of identifying the initial energy distribution of the excited molecules obtained by the CO₂ laser excitation.

In a recent study IR multiphoton excitation¹³ of CF₃I we have resolved the problem of the initial energy distribution for this molecule. Under certain experimental conditions, the energy distribution was shown experimentally to be narrow and localized near to the dissociation energy of the molecule. Starting with this energy distribution after the excitation laser pulse, the stepwise collisional deactivation of CF₃I can be followed by hot UV absorption spectroscopy of the excited molecules such as this was demonstrated before in Refs. 4 and 6-8. The calibration of the CF₃I UV absorption spectrum as a function of the average excitation energy $\langle E \rangle$ of the excited molecules has been done in separate studies^{13,14} such that an "internal energy thermometer"¹⁵ is available. Energy loss curves of CF₃I in collisions with partners of varying molecular complexity, therefore, became measurable in the present work. Particular emphasis was given to the question of the energy dependence of $\langle \Delta E \rangle$ as a function of the nature of the bath gas.

II. EXPERIMENTAL TECHNIQUE

Vibrationally highly excited CF₃I molecules were produced by irradiation with pulses from a TEA CO₂-laser operating at the 9R14 line at 1074.6 cm⁻¹. Single mode laser pulses of 20–50 ns length were produced with an intracavity absorption cell filled with CF₃Br and a plasma shutter. Amplification of the pulses was achieved in part of the experiments by a second CO₂ laser. Typical laser fluences for 50 ns pulses were 0.4 J/cm². The details of the laser operation were described in Ref. 13.

The stepwise energy loss of the excited CF₃I molecule in collisions with various bath gases was monitored via the time-dependent absorption signals in the UV of excited CF₃I molecules. Suitable mixtures of CF₃I (pressure in the range of 50 mTorr) and the bath gases Ar, propane, and octane (pressures in the range 1–10 Torr) were introduced into a cylindrical reaction cell (length 213 cm, diameter 2.6 cm). The excitation laser beam was transmitted along the axis through this cell beam-in-beam with the analysis light from a Xe-Hg high-pressure arc lamp. The analysis light was recorded in a monochromator-photomultiplier-transient digitizer combination. Averaging of up to 1000 shots was applied with an exchange of the gas mixture in the cell by a slow flow. All further details of the experiments have been described in Ref. 13.

III. ENERGY DEPENDENCE OF CF₃I UV ABSORPTION SPECTRA

The absorption-time profiles of CF₃I after the laser pulse were analyzed with respect to the stepwise decrease of the average energy $\langle E \rangle$ of the highly excited CF₃I via hot UV absorption spectroscopy. The energy dependence of the spectrum was derived via thermal excitation experiments in shock waves. Earlier experiments from Ref. 16 recently¹⁴ have been extended up to temperatures of about 1400 K where the average thermal vibrational energy of CF₃I reaches up to about 8400 cm⁻¹, i.e., almost one half of the dissociation energy $E_0 = (18\,180 \pm 330)$ cm⁻¹. The gap between $E_0/2$ and E_0 was bridged by a modified Sulzer-Wieland fit of the shock wave spectra following the expression for the absorption cross section,

$$\sigma(\nu, T) = \sigma_{\max}^0 \sqrt{\tanh(\theta_0/2T)} \times \exp \left[-\tanh\left(\frac{\theta_0}{2T}\right) \left(\frac{\nu - \nu_0}{\Delta\nu_0}\right)^2 \right] \quad (1)$$

with the parameters $\theta_0 = 409$ K, $\sigma_{\max}^0 = 8.05 \times 10^{-19}$ cm², $\Delta\nu_0 = 2370$ cm⁻¹, and $\nu_0(T) = (38\,017 - 417 \cdot T/300 \text{ K})$ cm⁻¹. Figure 1 shows the temperature-dependent CF₃I spectrum given by representation of Eq. (1). An extrapolation to the temperature of 3300 K, where the average thermal vibrational energy approaches the dissociation energy, is also given. It was shown in Ref. 13 that molecules showing after-pulse dissociation, whose energy, is close to the dissociation energy, have a spectrum which agrees very well the wavelength dependence of σ with the 3300 K spectrum. Converting the temperature T in Eq. (1) into the corresponding average vibrational energy $\langle E \rangle$, one obtains the required energy dependence of the spectrum such as done in

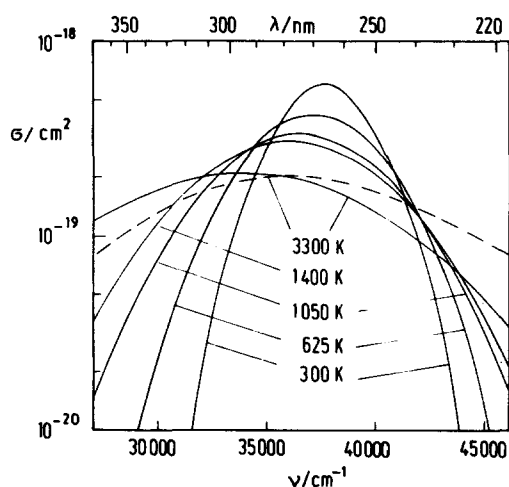


FIG. 1. Temperature dependence of the CF₃I UV spectrum representation of Eq. (1) based on shock wave experiments from Refs. 14 and 16; high-temperature extensions corresponding to CO₂-laser excitation (see Ref. 13).

earlier energy transfer studies.^{3,4,6,7,9} It should be emphasized that strongly bimodal energy dependences cannot be treated in this way using a common average energy. Instead the superposition of two different ensembles then has to be taken into account. This was observed in the very low pressure experiments with multiphoton excited CF₃I in part I.¹³ Our present observations were made mainly at relatively long wavelengths where only the hot CF₃I ensemble absorbs and a heating of cold CF₃I molecules did not contribute too much to the absorption under the chosen conditions.

The absorption cross sections over the wavelength range 265–365 nm have markedly different energy dependences. For the wavelengths 265, 295, 313, 334, and 365 nm, Figs. 2 and 3 show the results based on Fig. 1 and Eq. (1). By means

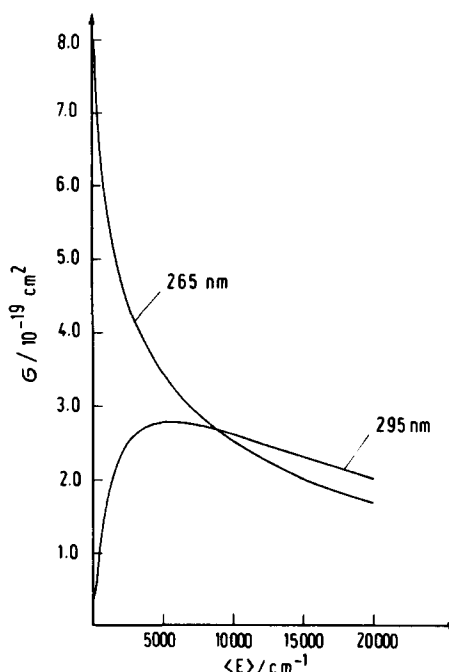


FIG. 2. Dependence of the absorption cross section of CF₃I on the temperature at $\lambda = 265$ and 295 nm.

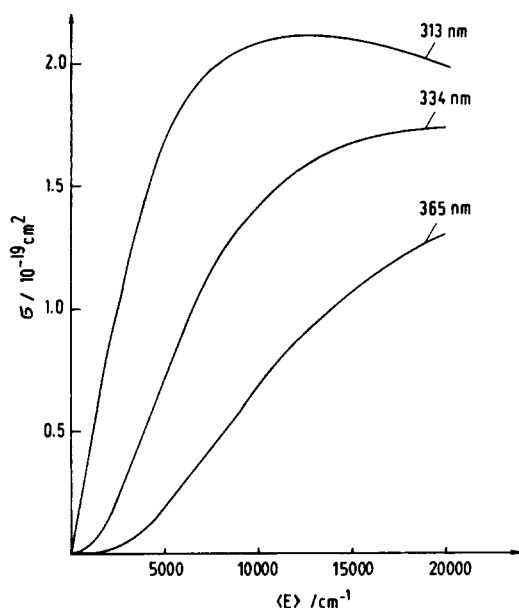


FIG. 3. As Fig. 2, for $\lambda = 313, 334,$ and 365 nm.

of these representations absorption-time profiles can be converted into average energy-time profiles. Heating up of the background of cold molecules can be taken into account most easily by the superposition of the spectra of two different ensembles. Observations at several wavelengths allow for an unambiguous assignment of the average energies of the two different ensembles.

IV. PRESSURE EFFECTS ON ABSORPTION-TIME PROFILES

There are a number of different pressure effects on the dynamic behavior of the IR multiphoton excitation of CF₃I such as discussed in Part I.¹³ In order to arrive at an undisturbed observation of the energy-loss profiles, the experimental conditions have to be chosen in a way which avoid complications from a superposition of these different effects. For example, one has to consider the quenching of after-pulse dissociation and the deactivation of excited states reached by the optical pumping during the pulse. On the other hand, collisions can improve the optical pumping process by breaking early bottleneck behavior and modifying the initial distribution. We discuss the conditions for these effects in the following. If a laser intensity of 8 MW cm^{-2} is chosen (0.4 J/cm^2 in a 50 ns pulse), the low-gas pressure of 300 mTorr quenches about 80% of the after-pulse dissociation such as shown in paper I.¹³ Since our collisional deactivation experiments have all been performed with about 10 times larger pressures, there was only the possibility for dissociation during the pulse but not after the pulse. In paper I,¹³ the pressure dependence of the absorbed total energy E_{abs} from the laser pulse as well as the pressure effect on the fraction α of highly excited molecules have been studied. The increases of E_{abs} and α , e.g., for pressures below 7 Torr of propane, were attributed to overcoming the early bottleneck. Working at pressure where this effect just starts, the effects on the distribution of excited molecules were

minimized. Compared to these collisional effects during the laser pulse, which enhance the effective pumping rate, collisional deactivation during the laser pulse was negligible. The contribution from the latter effect can be estimated on the basis of the Lennard-Jones collision frequencies. Using the Lennard-Jones parameters $\sigma = 4.90, 4.94, 3.47,$ and 7.02 \AA , and $\epsilon/k = 285, 274, 114,$ and 359 K for CF₃I, propane, Ar, and octane, one has Lennard-Jones collision frequencies of $9.60 \times 10^6, 1.58 \times 10^7, 9.76 \times 10^6,$ and $1.73 \times 10^7 \text{ Torr}^{-1} \text{ s}^{-1}$ for collisions of CF₃I with CF₃I, propane, Ar, and octane, respectively. At pressures in the range $2\text{--}5 \text{ Torr}$, therefore, CF₃I molecules on the average undergo only a single collision during laser pulses of $20\text{--}50 \text{ ns}$ length.

According to the given estimates and observations from paper I, one can assume that the initial energy distribution of the hot molecules after the pulse under our conditions is narrow (half-width $< 1000 \text{ cm}^{-1}$) and localized near the dissociation energy at $18\,180 \text{ cm}^{-1}$. At the chosen pressures, above 1 Torr , there is no after pulse dissociation such that all changes of the absorption-time profiles can be attributed to the collisional deactivation process. Figure 4 shows a typical absorption-time profile corresponding to the energy loss of the excited molecules such as recorded at 334 nm . At this wavelength, the heating of the background of cold CF₃I molecules during the energy loss of the hot CF₃I does not contribute to the absorption signal. Observations at shorter wavelengths indicate that there is a heating of cold CF₃I. Figure 5 shows a signal recorded at 313 nm . The figure includes the profile, which was constructed for the energy loss of the hot CF₃I molecules by using observations at longer wavelengths where no signal from the heating of cold CF₃I contributes. There is very good agreement for the first part of the process, until the energy of the hot molecules has decayed to about 3000 cm^{-1} (reached after about $3 \mu\text{s}$).

V. AVERAGE ENERGIES TRANSFERRED PER COLLISION

Having converted the absorption-time profiles like Fig. 4 into energy-loss profiles, i.e., $\langle E \rangle$ as a function of the number of collisions $Z_{\text{LJ}} \cdot P \cdot t$ ($P = \text{bath gas pressure}, t = \text{time}$), we evaluate them following the relationship¹⁷

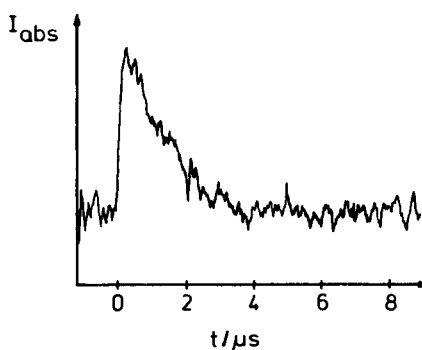


FIG. 4. Absorption-time profile of CF₃I at $\lambda = 334 \text{ nm}$. Collisional deactivation by 3 Torr of propane after IR multiphoton excitation (pulse width 50 ns , 0.4 J/cm^2) of 70 mTorr of CF₃I.

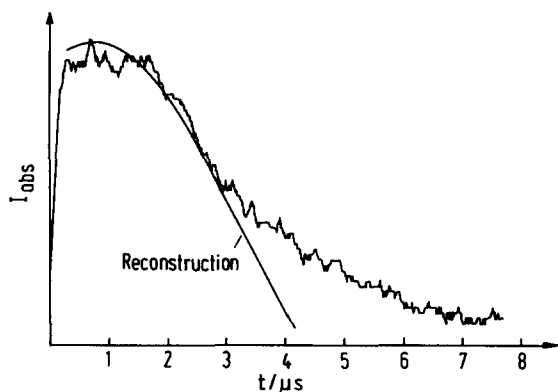


FIG. 5. Absorption-time profile of CF₃I at $\lambda = 313$ nm. Collisional deactivation by 1.5 Torr of propane after IR multiphoton excitation (16 MW/cm²) of 120 mTorr of CF₃I (deviations between measured and reconstructed signal due to background heating, see the text).

$$\frac{d\langle E \rangle}{Z_{LJ} P dt} = \langle \Delta E \rangle. \quad (2)$$

The energy dependence of $\langle \Delta E \rangle$ is sufficiently weak to allow for the application of Eq. (2) such as demonstrated in Ref. 17 by a comparison of the solution of Eq. (2) with a complete numerical solution of the master equation. We assume that rotational effects of collisional energy transfer¹⁸ do not lead to particular complications. The experimental signals were fitted numerically to the solution of Eq. (2) resulting in the dependence of $\langle \Delta E \rangle$ on $\langle E \rangle$. Figures 6–8 show the curves obtained for the bath gases Ar, propane, and octane. Table I gives numerical $\langle \Delta E \rangle$ values for selected energies $\langle E \rangle$; the table also includes the pressure ranges of the experiments in the different bath gases.

Figs. 6–8 show characteristic differences between the three bath gases. Whereas

$$\langle \Delta E \rangle \propto \langle E \rangle^n, \quad (3)$$

appears to be valid with $n = 1$ for CF₃I + propane and

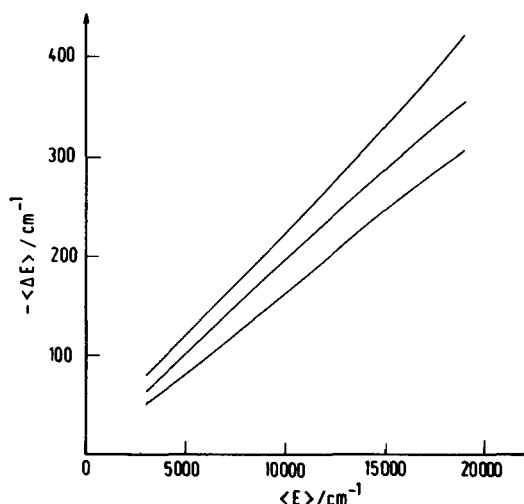


FIG. 7. As Fig. 6, collisions of CF₃I with propane.

CF₃I + octane collisions over the full energy range of our studies (3000–18 000 cm⁻¹), there is clearly a nonlinear energy dependence of $\langle \Delta E \rangle$ for CF₃I + Ar collisions. In the latter case, n approaches unity at high energies; a value $n > 1$ is found for energies below 10 000 cm⁻¹. The dashed line in Fig. 8 would correspond to a value of $n = 3/2$ such as found¹¹ for SF₆ + SF₆ collisions at $\langle E \rangle \leq 5000$ cm⁻¹. Our measurements could not be extended reliably to too low energies for several reasons: the heating of the background gas then led to a too strong superposition of the spectra from the initially hot and cold ensembles; the state distributions after a long deactivation process tend to become too broad; the final equilibrium temperature exceeds room temperature; diffusive processes start to mix cold gas outside the light beams with the observed gas volume. Therefore, experiments with lower initial excitation, using lower laser intensities would be required in order to fill the gap of the measurements at low energies $\langle E \rangle$. Nevertheless, the difference between the measurements with Ar and with propane and

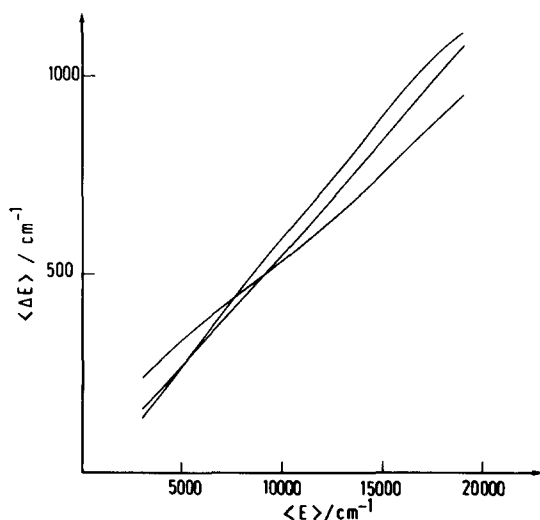


FIG. 6. Average energy $\langle \Delta E \rangle$ transferred in collisions of highly excited CF₃I with octane (laser fluence 0.4 J/cm², the different curves correspond to fits to individual experiments).

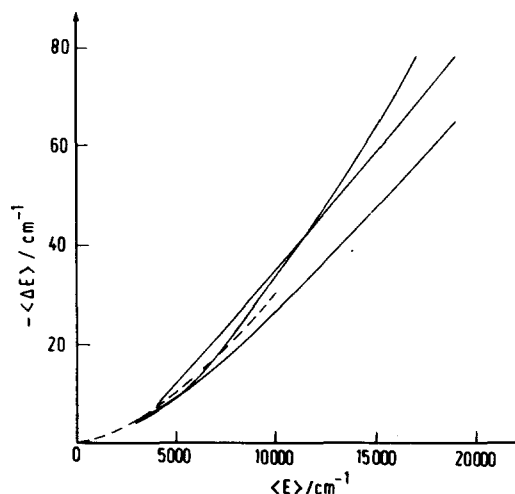


FIG. 8. As Fig. 6, collisions of CF₃I with argon (---; fictitious energy dependence of $\langle \Delta E \rangle \propto \langle E \rangle^{3/2}$ for $\langle E \rangle \leq 10\,000$ cm⁻¹).

TABLE I. Average energies $\langle \Delta E \rangle$ (in cm⁻¹) transferred in collisions of excited CF₃I (average energy $\langle E \rangle$) with various collision partner.

| $\langle E \rangle$ /cm ⁻¹ | Ar (9 Torr) | Propane (1.5–3 Torr) | Octane (0.7–1.5 Torr) |
|---------------------------------------|----------------|-------------------------|--------------------------|
| 5 000 | 10 | 110 | 280 |
| 10 000 | 40 | 210 | 570 |
| 15 000 | 70 | 320 | 880 |

octane at low energies is clearly outside the range of these possible experimental complications.

VI. DISCUSSION

For energies $\langle E \rangle$ in the range 15 000–20 000 cm⁻¹, i.e., close to the dissociation energy of CF₃I, the derived $\langle E \rangle$ values approach the “universal” values such as observed now for a fairly large group of excited polyatomic molecules. Table II compares the present $\langle \Delta E \rangle$ values for $\langle E \rangle = 18\,000$ cm⁻¹ and the collision partners Ar, propane, and octane with the corresponding values for other excited molecules. The general agreement indeed reveals a surprisingly “universal” character of the $\langle \Delta E \rangle$ values which presently is not yet understood theoretically. One should emphasize that all $\langle \Delta E \rangle$ values have been derived relative to Z_{LJ} as a reference collision frequency. In reality the experiments only lead to the product $Z_{LJ} \langle \Delta E \rangle$.

With regard to the absolute values of $\langle \Delta E \rangle$ near to the dissociation energy at energies of the order of 20 000 cm⁻¹, the present experiments do not provide new information. CF₃I collisions here just follow the general trends of uniform $\langle \Delta E \rangle$ values from excited triatomic to excited large polyatomic molecules. The energy dependence of $\langle \Delta E \rangle$, however in an interesting way reveals the transition between the small molecule case of $\langle \Delta E \rangle \propto \langle E \rangle^2$ and the large molecule case of $\langle \Delta E \rangle \propto \langle E \rangle$ (at low energies $\langle E \rangle$). The present system approaches the small molecule behavior for the inefficient collider Ar whereas large molecule behavior is established for the more efficient colliders propane and octane. The latter aspect of the present work will be discussed in more detail in the following.

TABLE II. Average energies $\langle \Delta E \rangle$ (in cm⁻¹) transferred in collisions of various excited molecules with Ar, propane, heptane, and octane.

| Excited molecule | Ar | Propane | Heptane | Octane | $\langle E \rangle$ /cm ⁻¹ | Reference |
|-----------------------|-----|---------|---------|--------|---------------------------------------|-----------|
| CF ₃ I | 70 | 320 | ... | 880 | 15 000 | This work |
| CS ₂ | 8 | 580 | 1620 | ... | 20 000 | 7 |
| CS ₂ | 24 | 1750 | 4200 | ... | 36 000 | 7 |
| SO ₂ | 7 | 490 | ... | ... | 20 000 | 7 |
| SO ₂ | 40 | 3160 | 3320 | ... | 45 600 | 7 |
| Azulene | 86 | 450 | ... | 724 | 15 000 | 6 |
| Azulene | 210 | 770 | ... | 1170 | 30 600 | 6 |
| Toluene | 130 | 520 | 930 | 990 | 52 000 | 4 |
| Ethylcycloheptatriene | 180 | 530 | ... | 1220 | 41 600 | 4 |

The proportionality between $\langle \Delta E \rangle$ and the energy $\langle E \rangle$, which at not too high energies is observed in collisions of excited large polyatomic molecules, corresponds to the results from classical trajectory calculations such as described in Refs. 3 and 18–24. The deviation from the proportionality, i.e., a stronger decrease of $\langle \Delta E \rangle$ with decreasing energy $\langle E \rangle$, in Ref. 3 was attributed to an increasing sparsity of the vibrational quasicontinuum with decreasing energy. Quantum effects selecting specific deactivation pathways, propensity rules, and the absence of the typical high-energy possibility of transferring essentially arbitrary amounts of energy, with decreasing energy become increasingly important. Various aspects of energy transfer in this low-energy range have been discussed, e.g., in Refs. 25–27. Since the present experiments are not characterized by the selection of individual state-to-state transitions but by the global energy loss from a broader distribution of excited states, it does not appear appropriate here to enter into an investigation of individual quantum effects. Instead, we try to relate the deviations from a $\langle \Delta E \rangle \propto E$ dependence to more global aspects of the system.

The most important result of this work lies in the observation that $\langle \Delta E \rangle \propto \langle E \rangle$ is found for the more efficient colliders propane and octane whereas marked deviations from this law occur for collisions with argon. This points to a conclusion that a nonlinearity of the $\langle \Delta E \rangle - \langle E \rangle$ dependence *cannot* be related *only* to properties of the excited molecule such as its density of states, level distribution or onset of the vibrational quasicontinuum. Instead, the properties of the bath gas, such as, e.g., the value of $\langle \Delta E \rangle$, also play an important role.

It appears difficult to draw similar conclusions from the available experiments on energy transfer in SF₆ + SF₆, and SF₆ + Ar collisions from Refs. 11, 12, 28, and 29. First, the $|\langle \Delta E \rangle|$ values for SF₆ + Ar collisions from Ref. 28 are much larger than those measured in Refs. 12 and 29. The experiments from Ref. 12 have led to $\langle \Delta E \rangle \approx -8$ cm⁻¹ at $\langle E \rangle = 20\,000$ cm⁻¹, appearing thus unrealistically low in comparison to the data from Refs. 3–10. Furthermore, even with the larger $|\langle \Delta E \rangle|$ values (-6 cm⁻¹ at $\langle E \rangle = 5000$ cm⁻¹) from Ref. 28, one would need at least a $\langle \Delta E \rangle \propto \langle E \rangle^2$ dependence up to $\langle E \rangle \approx 20\,000$ cm⁻¹ to reach $\langle \Delta E \rangle$ values of the order of -100 cm⁻¹ typical for this energy range. Similar remarks apply to the SF₆ + SF₆ results of $\langle \Delta E \rangle = -7$ cm⁻¹ at $\langle E \rangle = 5000$ cm⁻¹ from Ref. 11. This would place excited SF₆ much closer to the examples of excited triatomic molecules for which $\langle \Delta E \rangle \propto \langle E \rangle^2$ is approximately valid up to energies of the order $\langle E \rangle = 30\,000$ cm⁻¹. The present CF₃I results, however, show that CF₃I is closer to the examples of excited polyatomics such as azulene or toluene. At present, an unambiguous explanation of the different behavior of CF₃I and SF₆ cannot be given. One cannot rule out experimental problems in the CO₂-laser excitation experiments. One obvious uncertainty concerns the initial distribution of excited states reached by the CO₂ laser pulse. In the present work, this distribution could be identified as being strongly bimodal with one hot ensemble localized at energies near to the dissociation energy. From the absorbed total energy one would have estimated a much smaller average excitation energy. In the SF₆ excitation ex-

periments so far no direct analysis of the initial energy distribution was possible. Conclusions based on the total absorbed energy and assuming the collisional deactivation of a single ensemble of this average energy only could be false, since they would underestimate the initial energy of the hot ensemble if a strongly bimodal distribution would have been produced. Different laser pumping conditions then also could have resulted in different initial energies of the hot ensemble. As long as these problems are not clarified, the differences between the CF₃I and SF₆ experiments should not be overinterpreted.

In summary, we have shown that IR multiphoton excitation experiments can yield useful collisional energy transfer data, under the condition that the initial distributions reached by the laser pulse can be characterized sufficiently well.

ACKNOWLEDGMENTS

Discussions of this work with R. J. Gordon, K. Luther, and G. Schatz as well as financial support by the Deutsche Forschungsgemeinschaft (SFB 93 "Photochemie mit Lasern") are gratefully acknowledged.

¹D. C. Tardy and B. S. Rabinovitch, *Chem. Rev.* **77**, 396 (1977).

²M. Quack and J. Troe, *Gas Kinetics and Energy Transfer*, Vol. 2 (The Chemical Society, London, 1977), p. 175.

³H. Hippler and J. Troe, in *Gas Phase Bimolecular Processes*, edited by J. E. Baggott and M. N. Ashfold (The Royal Society of Chemistry, London, 1989).

⁴H. Hippler, J. Troe, and H. J. Wendelken, *Chem. Phys. Lett.* **84**, 257 (1981); *J. Chem. Phys.* **78**, 6709, 6718 (1983); M. Heymann, H. Hippler, and J. Troe, *ibid.* **80**, 1853 (1984).

⁵M. Rossi, J. R. Pladziewicz, and J. R. Barker, *J. Chem. Phys.* **78**, 6695 (1983); J. R. Barker and R. E. Golden, *J. Phys. Chem.* **88**, 1012 (1984); J. H. Shi and J. R. Barker, *J. Chem. Phys.* **88**, 6219 (1988); J. R. Barker, *J. Phys. Chem.* **88**, 11 (1985).

⁶H. Hippler, L. Lindemann, and J. Troe, *J. Chem. Phys.* **89**, 1698 (1985); H. Hippler, B. Otto, and J. Troe, *Ber. Bunsenges. Phys. Chem.* **93**, 428 (1989).

⁷J. E. Dove, H. Hippler, H. J. Plach, and J. Troe, *J. Chem. Phys.* **81**, 1209 (1984); M. Heymann, H. Hippler, H. J. Plach, and J. Troe, *ibid.* **87**, 3867 (1987); M. Heymann, H. Hippler, D. Nahr, H. J. Plach, and J. Troe, *J. Phys. Chem.* **92**, 5507 (1988).

⁸T. Ichimura, Y. Muri, M. Nakashima, and K. Yoshihara, *J. Chem. Phys.* **83**, 117 (1985); T. Ichimura, M. Takahashi, and Y. Muri, *Chem. Phys.* **114**, 116 (1987); N. Nakashima and K. Yoshihara, *J. Chem. Phys.* **79**, 2727 (1983).

⁹M. Damm, H. Hippler, and J. Troe, *J. Chem. Phys.* **88**, 3564 (1988).

¹⁰H. G. Löhmannsröben and K. Luther, *Chem. Phys. Lett.* **114**, 473 (1988); K. Luther and K. Reihs, *Ber. Bunsenges. Phys. Chem.* **92**, 422 (1988); (unpublished).

¹¹W. Braun, M. D. Scheer, and R. J. Cvetanovic, *J. Chem. Phys.* **88**, 3715 (1988); W. Braun, M. D. Scheer, and V. Kaufman, *J. Res. Natl. Bur. Stand.* **91**, 313 (1986).

¹²K. M. Beck and R. J. Gordon, *J. Chem. Phys.* **87**, 5681 (1987); R. J. Gordon, *Comments At. Mol. Phys.* **21**, 123 (1988).

¹³B. Abel, B. Herzog, H. Hippler, and J. Troe, *J. Chem. Phys.* **91**, 890 (1989).

¹⁴B. Abel, L. Brouwer, B. Herzog, H. Hippler, and J. Troe, *Chem. Phys. Lett.* **127**, 541 (1986); H. Hippler, H. A. Olschewski, J. Troe, and J. Willner, *Z. Phys. Chem. NF* (in press).

¹⁵L. Brouwer, H. Hippler, L. Lindemann, and J. Troe, *J. Phys. Chem.* **89**, 4608 (1985).

¹⁶L. Brouwer and J. Troe, *Chem. Phys. Lett.* **82**, 1 (1981).

¹⁷J. Troe, *J. Chem. Phys.* **77**, 3485 (1982).

¹⁸H. W. Schranz and J. Troe, *J. Phys. Chem.* **90**, 6168 (1986).

¹⁹M. Bruehl and G. Schatz, *J. Phys. Chem.* **92**, 7723 (1988).

²⁰N. J. Brown and J. A. Miller, *J. Chem. Phys.* **80**, 5568 (1984).

²¹M. B. Grinchak, A. A. Levitzky, L. S. Polak, and S. Ya. Umanski, *Chem. Phys.* **88**, 365 (1984).

²²W. L. Hase, N. Date, L. B. Bhuiyan, and D. G. Buckowski, *J. Chem. Phys.* **89**, 2502 (1985).

²³A. Gelb, *J. Chem. Phys.* **89**, 4189 (1985).

²⁴K. F. Lim and R. G. Gilbert, *J. Chem. Phys.* **84**, 6129 (1986).

²⁵D. C. Clary, *J. Am. Chem. Soc.* **106**, 970 (1984); *J. Chem. Phys.* **86**, 802, 813 (1987).

²⁶K. Y. Tang and C. S. Parmenter, *J. Chem. Phys.* **78**, 3922 (1983); D. J. Krajnovich, C. S. Parmenter, and D. C. Catlett, *Chem. Rev.* **87**, 237 (1987).

²⁷S. H. Kable, J. W. Thoman, and A. E. W. Knight, *J. Chem. Phys.* **88**, 4748 (1988).

²⁸M. Lenzi, E. Molinari, G. Picciacchia, V. Sessa, and M. L. Terranova, *Chem. Phys.* **108**, 167 (1986); *Spectrochim. Acta Part A* **43**, 137 (1987).

²⁹S. A. Akhmanov, V. M. Gordienko, V. V. Lazarev, A. V. Mikheenko, and V. Ya. Pachenko, *Sov. Phys. JETP* **51**, 1087 (1980).