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Collisional energy transfer in unimolecular reactions induced by vibrational overtone excitation

J. E. Baggott and D. W. Law
Department of Chemistry, University of Reading, Whiteknights, P.O. Box 224, Reading RG6 2AD, United Kingdom

The kinetics of the gas phase isomerisation of cyclobutene initiated by direct single photon excitation of C–H stretching overtones have been studied and the observed behavior has been interpreted using a treatment which combines RRKM theory and models accounting for weak intermolecular energy transfer. Results obtained from the excitation of five different overtone states spanning an energy range of 5070 cm^{-1} have allowed us to examine the form of the dependence on energy of the energy transfer step sizes $\langle \Delta E \rangle$ deduced from numerical solutions of the collisional master equation using an exponential-down model, for the collider gases cyclobutene, SF_6, CHF_3, CH_4, CO_2, H_2, CO, N_2, Ar, and He. Our calculations indicate very small energy transfer step sizes, particularly for the most inefficient collider molecules. We discuss the factors which might contribute to the determination of low values for $\langle \Delta E \rangle$ and the sensitivity of the master equation calculations to details of the RRKM model. Our results, when expressed in terms of absolute changes in the magnitudes of $\langle \Delta E \rangle$ as a function of energy, appear to be in agreement with the recent direct studies of Hippler *et al.* [J. Chem. Phys. **83**, 3906 (1985)] for a number of collider molecules over the energy range of the present work. Mean collision efficiency parameters calculated directly from the slopes of the Stern–Volmer plots are shown to be linearly correlated with mean values of $\langle \Delta E \rangle$. In future studies of unimolecular reactions induced by overtone excitation, our results should enable full account of weak collisional energy transfer to be taken, allowing for a more rigorous comparison of experimental energy-specific rate constants with RRKM predictions.

INTRODUCTION

The description of highly excited stretching vibrational states of X–H bonds (X = C, N, O, etc.) as local modes has been accepted for many years and has stimulated considerable theoretical and experimental study. In this description any equivalent X–H bonds in a polyatomic molecule are considered as independent morse oscillators. In the region of the bond stretching fundamentals, interbond coupling terms give rise to the observation of normal modes of different symmetry combinations. As the vibrational excitation is increased so does the contribution from morse anharmonicity with the result that the interbond coupling becomes insignificant compared to the increasing energy gap between the states with all of the excitation in one bond and combinations in which the excitation is distributed between two or more bonds. At a certain level of excitation, which depends on the ratio of interbond coupling to morse anharmonicity,[1] the system collapses to a single optically accessible state which has an energy much lower than any combinations. Thus, overtone spectra show features that are assigned as n quanta of excitation in a single X–H bond.[2]

The localization of excitation energy implied by the local mode model led Henry[3] to suggest that such excited states might not satisfy the requirements of one of the assumptions fundamental to the development of RRKM theory concerned with intramolecular energy flow. For this assumption to be valid, complete energy exchange must be established between the active modes of a unimolecular reac-

tant on timescales shorter than that characteristic of reaction. Although in principle it is possible to apply RRKM theory with some modes assigned as "inactive" in general practice all modes are usually considered and the assumption is therefore extended to one of rapid and complete redistribution of excitation energy through all of the molecular degrees of freedom. For a given postulated activated complex the magnitude of the energy-specific rate constant $k(E^*)$ depends only upon the total energy content and not on the nature of preparation of the excited molecule. Local modes appear to offer the possibility of defeating intramolecular vibrational energy redistribution (IVR) and of obtaining a much sought-after goal of mode-selective photochemistry.

Such speculation concerning the nature of highly excited vibrational overtone states prompted numerous studies of the kinetics of gas-phase unimolecular reactions induced by direct, one-photon overtone excitation. Reddy and Berry[4] applied intracavity dye laser photoacoustic techniques to the study of vibrational overtones and used the high circulating light intensities within the cavity of a cw dye laser to initiate isomerisation with measureable quantum yields. These steady-state experiments were followed rapidly by novel time-resolved studies which utilized chemiluminescence[5] or product laser-induced flourescence[6] to measure overtone spectra and product appearance rates. The field has been reviewed recently by Crim.[7] The experimental evidence collected thus far appears to confirm the validity of the assumption of rapid IVR although some exceptions have been not-

ed.[8,9] Lifetimes for energy redistribution of the order of 1 ps or less are, of course, known from chemical activation studies,[10] and recent advances in the interpretation of vibrational overtone spectra are pointing towards a similarly rapid loss of initial state probability for local modes contaminated by coupling to other molecular vibrations via Fermi resonance.[11,12] Alternatively, the presence of contaminating vibrations means that the initially prepared state is a somewhat ill-defined mixture in which the excitation energy is already partially (or completely) "redistributed."

The purpose of the present paper is to address one specific problem associated with the study of unimolecular reactions induced by overtone excitation which has received relatively little attention. Steady-state experiments involving intracavity cw dye laser excitation have been interpreted previously in terms of simple Stern–Volmer kinetics with no attempt to take account of the effects of inefficient collisional energy transfer. Thus, measurements of the reciprocal quantum yield as a function of gas pressure have been used to determine $k(E^*)$ values using the relation

$$\Phi^{-1} = 1 + \frac{Z_{AA}[A]}{k(E^*)}. \tag{1}$$

Here Z_{AA} is the bimolecular rate constant for the (single step) collisional deactivation of the vibrationally excited reactant and $k(E^*)$ is the rate constant for unimolecular reaction at the energy E^*, usually taken as the photon energy plus $\langle E_{vib}\rangle$, the average vibrational energy of the ground state molecule at the temperature of the experiment. [A] represents the pressure of collider gas; in this case unexcited reactant. Equation (1) or an equivalent expression has been used by numerous authors to determine experimental $k(E^*)$ values for comparisons with RRKM predictions. However, for many of the unimolecular reactions studied to date, the energies deposited in the reactant by overtone excitation have exceeded the threshold to reaction by an amount recognized to be beyond the capabilities of the bath gas molecules to remove in a single collision. Neglect of such effects results in the determination of inflated $k(E^*)$ values.

We have examined in detail the effects of weak collisional energy transfer in the isomerisation kinetics of cyclobutene following excitation of five different C–H stretching overtone states. Cyclobutene is a particularly favorable example for this kind of study since it undergoes isomerization with a very low threshold (11 236 cm^{-1}) and shows no tendency to react on surfaces. In the study of Jasinski et al.,[13] this molecule was shown to behave statistically in its overtone-induced reaction in that $k(E^*)$ varied monotonically with excitation energy. Small deviations in the magnitudes of the $k(E^*)$ values compared to RRKM theory estimates were noted[13] but, as we will show, these can be traced to the effects of inefficient collisional energy transfer.

The distribution of overtone states in regions of the near IR/visible accessible with an Ar$^+$ laser pumped cw dye laser has allowed us to prepare excited molecules with a very precisely known internal energy content varied over a wide range of energies. We are thus in a position to determine the nature of the variation of collisional energy transfer step size $\langle \Delta E\rangle$ as a function of the excitation energy for a number of different collider gases. Recent time-resolved experiments

by Barker and Troe and their co-workers[14,15] have produced conflicting evidence concerning the dependence of $\langle\Delta E\rangle$ values on energy. These studies involved the direct observation of energy removal from vibrationally excited ground state molecules formed by internal conversion from electronically excited states[14] or by isomerization of highly excited precursors.[15] In the present study we have the advantage that highly vibrationally excited molecules are prepared by direct excitation of overtone states combined with the disadvantage of having to deal with steady-state kinetics. Indeed, our work parallels the earlier chemical activation studies of Rabinovitch and his group[10] with the difference that our initial internal energy distribution is slightly better determined.

EXPERIMENTAL

Cyclobutene synthesis

Cyclobutene was prepared from cyclo-octatetraene using the method of Cope et al.[16] by our colleague John Warrington. Analysis of the products by gas chromatography (see below) revealed the presence of some buta-1,3-diene impurity which was removed by prolonged heating to 50 °C with tetracyanoethylene. The product of the Diels–Alder combination of buta-1,3-diene and tetracyanoethylene exhibits a negligible vapor pressure and so the cyclobutene could be separated by trap-to-trap distillation at liquid nitrogen temperatures. Subsequent analysis showed that the buta-1,3-diene impurity had been reduced to ~0.1% or less by this technique. FTIR spectra of gas-phase cyclobutene showed no additional nonhydrocarbon impurities.

Sample handling was performed on a grease-free vacuum system capable of being pumped down to ~2×10^{-5} Torr. The cyclobutene was degassed by exhaustive freeze-pump–thawing at regular intervals during the course of the experiments. Pressures were measured using two Baratron 200 Series pressure transducers (MKS Instruments) with ranges 0–10 and 0–1000 Torr.

Overtone spectroscopy

Details of the intracavity cw dye laser photoacoustic arrangement used to measure C–H stretching overtones in the near IR/visible regions have been described previously.[12,17] Briefly, a Coherent Inc. Innova 90-5 Ar$^+$ laser was used to pump a CR 699-01 ring dye laser operated in a standing wave configuration with the following dyes: styryl 9M 11 400–12 500 cm^{-1}, pyridine 1 12 900-14 600 cm^{-1}, and rhodamine 6G 15 300-17 100 cm^{-1}. A nonresonant photoacoustic cell containing a Knowles BT 1759 electret microphone was placed inside the dye laser cavity and the resulting acoustic signal was detected by a model 5205 lock-in amplifier (EG&G). Mechanical modulation of the excitation was achieved by chopping the Ar$^+$ laser pump beam. Wavelength tuning of the dye laser and signal collection and processing were fully microcomputer controlled. The tuning element used was a 3-plate birefringent filter affording a spectral resolution of ~1 cm^{-1} in the rhodamine 6G region. Spectra were calibrated for wavelength using signals derived from a Ne filled hollow cathode lamp. All spectra were normalized for variation in the dye laser power as a function of

wavelength. The reader is referred to an earlier publication[12] for a presentation and interpretation of the overtone spectra.

Calibration of the absorption cross sections at the different photolysis wavelengths was achieved using two methods. For the $v = 5$ and 6 C–H stretching overtone bands at 13 440, 14 123, 15 718, and 16 601 cm^{-1}, peak absorption cross sections were obtained by comparison with the values for the $v = 5$ and 6 C–H overtones of methane reported by Giver.[18] Mixtures containing equal partial pressures of methane and cyclobutene were prepared and their photoacoustic spectra recorded. The methane overtone bands at 727.7 and 619.2 nm fall between the $v = 5$ and 6 methylenic and olefinic C–H overtones in cyclobutene (see the spectra reported in Ref. 12) and computer deconvolution assuming Lorentzian band profiles was used to compare the peak maxima. The methane overtones show some partially resolved rotational structure at the dye laser resolution and so this method of calibration should be regarded with some caution. Wong and Moore[19] have discussed the problems but at present we have no alternative reference standard.

For the olefinic $v = 4$ C–H overtone at 11 531 cm^{-1} the calibration method using methane reference data could not be used as the $v = 4$ C–H stretch overtone of CH$_4$ was beyond the long wavelength limit of the laser dye. In addition, the $v = 4$ C–H overtone of benzene, for which Reddy et al.[20] have provided an estimate of the absorption cross section (calibrated, in turn, against methane) was too strongly overlapped by the olefinic C–H overtone in cyclobutene to allow us to use the method described above. Instead, we recorded the peak photoacoustic signals from separate samples of benzene and cyclobutene at equal pressures. Assuming identical irradiation geometries, these signals are related by the absorption cross sections at the peak of the overtone transitions, the specific heat capacities at constant volume for the two gases and the intracavity laser powers at the wavelengths of peak absorption.[19] We used estimates of the heat capacities provided by Stull et al.[21] and the data of Reddy et al.[20] to determine the absorption cross section for cyclobutene at 11 531 cm^{-1}.

To enable the absorption cross sections determined using the above calibration methods to be compared with those derived from the kinetic data (see Results section below) it was necessary to obtain estimates of the transmittances of the end mirrors used to close the dye laser cavity and through which the laser power was monitored. These mirrors were coated to produce maximum reflectance over the wavelength ranges of the various laser dyes used with the consequence that their transmittances were determined with some difficulty. For the wavelength regions covered by pyridine 1 and rhodamine 6G the ratio of the light intensities incident on and transmitted by the total reflectors gave the transmittances directly. For these determinations, the dye laser (operated with a normal output coupler mirror) was tuned to the photolysis wavelengths and the transmittances of the extracavity radiation by the total reflectors was measured. Transmittances ranging from 1×10^{-4} to 1×10^{-3} were obtained. For the experiments involving styryl 9M laser dye a normal output coupler mirror was used for which a transmittance of 0.02 was quoted.[22]

Photolysis and end product analysis

Once the overtone spectra had been determined the dye laser was tuned to the various band maxima and timed photolyses of samples of cyclobutene and cyclobutene/buffer gas mixtures were performed. A separate reaction cell was constructed for this purpose. At the end of a photolysis period the reaction cell was connected to the inlet port of a Valco zero-dead-volume gas sampling valve on a Perkin–Elmer model 8310 gas chromatograph fitted with a flame ionization detector. The sampling valve and connector were evacuated before the contents of the reaction cell were allowed to diffuse into the sample loop. A 6 ft. × 1/8 in. stainless steel column of picric acid on Graphpak (Alltech Associates) maintained at 30 °C with He carrier gas provided for suitable separation of cyclobutene and its isomerisation product buta-1,3-diene. Electronic integration was used to determine the peak areas. The sum of the peak areas was used as a measure of the initial cyclobutene concentration A_0 after correction for the slightly different detection sensitivities of cyclobutene and buta-1,3-diene. The phenomenological rate constant for isomerisation induced by overtone excitation was calculated using the expression
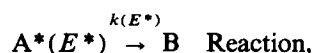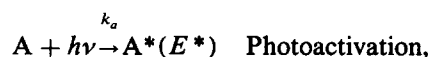
$$k_{obs} = \frac{-\ln(A/A_0)}{pt}, \qquad (2)$$

where A is the peak area of the buta-1,3-diene product and p and t are the extracavity laser power and photolysis time, respectively. No evidence was obtained for reaction products other than buta-1,3-diene.

RESULTS
Kinetics

The simplest kinetic scheme that can be proposed for a unimolecular reaction initiated by photoexcitation is as follows:

$$A + h\nu \xrightarrow{k_a} A^*(E^*) \quad \text{Photoactivation,}$$

$$A^*(E^*) + A \xrightarrow{Z_{AA}} A + A \quad \text{Collisional deactivation,}$$

$$A^*(E^*) \xrightarrow{k(E^*)} B \quad \text{Reaction,}$$

for which a steady-state analysis gives

$$-\frac{d[A]}{dt} = k[A][h\nu],$$

$$k = \frac{k_a k(E^*)}{k(E^*) + Z_{AA}[A]} = pk_{obs}. \qquad (3)$$

Equation (3) can be rearranged to give

$$k^{-1} = k_a^{-1} + \frac{Z_{AA}[A]}{k_a k(E^*)} \qquad (4)$$

or[12]

$$\Phi^{-1} = k_a/k = 1 + \frac{Z_{AA}[A]}{k(E^*)}. \qquad (5)$$

This last expression indicates that the reciprocal quantum yield for overtone-induced isomerization should vary linear-

ly with the pressure of the reactant with a slope determined by the rate constant for reaction at the energy of the overtone vibration. This is illustrated in Fig. 1 which shows the results of reciprocal quantum yield determinations for pure cyclobutene plotted against collision frequency Z ($= Z_{AA}[A]$) at five different overtone energies. It should be noted that for clarity of presentation not all of the data at the very lowest or highest cyclobutene pressures are shown in Fig. 1. Procedures used in the estimation of Z_{AA} are described below. The slopes of the plots vary markedly with energy, reflecting changes in $k(E*)$ of almost two orders of magnitude in total.

Before the bulk of the experimental data was collected the following experimental checks for artifacts were performed: (i) on an occasional basis throughout the study samples of cyclobutene were sealed in the reaction cell and left for several hours (sometimes overnight) at room temperature before gas chromatography analysis to determine the extent of any thermal contribution to the observed buta-1,3-diene yields. No additional product above the small amount already present as an impurity was observed. The cyclobutene itself was stored as a liquid at room temperature and showed no signs of slow isomerization under these conditions. (ii) Some photolysis experiments were performed with the dye laser wavelength tuned to a region in which no photoacoustic signal was observed. The resulting photoisomerization yields were found to be negligible on the timescale of a typical experiment. (iii) Isomerization rate constants were determined at an excitation wavelength of 16 601 cm^{-1} as a function of photolysis time and laser power over the ranges 1200-7200 s and 0.13-9.00 mW (measured extracavity) for a constant cyclobutene pressure of 10 Torr, resulting in percent conversions in the range 1.6-56.2. These measurements indicated that the phenomenological expression used to calculate the rate constants, Eq. (2), was obeyed except at the very longest photolysis times. Accordingly, photolysis times were restricted to 3600 s or less.

Determination of k_a

From Eq. (5) it can be seen that calculation of the reciprocal quantum yield values requires prior knowledge of the excitation rate constants, k_a. In principle, these can be determined from the intercepts of plots of k_{obs}^{-1} vs pressure at each photolysis wavelength [Eq. (4)].[12,17] However, for the longest photolysis wavelengths the slopes of the plots of k_{obs}^{-1} vs. pressure are very large (cf. Fig. 1) with the result that the magnitudes of the intercepts are poorly determined and subject to considerable error.

We define a slightly modified excitation rate constant k_a', given by

$$k_a' = \frac{k_a[hv]}{p} = \frac{\sigma c[hv]}{p},$$

where $[hv]$ is the photon density in the reaction cell and σ is the overtone absorption cross section at the photolysis wavelength. The units of k_a' are W^{-1} s^{-1} and the ratio k_a'/k_{obs} gives the reciprocal quantum yield directly. The quantity $[hv]$ is given by [12,23]

$$[hv] = \frac{2\lambda p}{hc^2 T A_{eff}},$$

where p is the extracavity laser power, T is the transmittance of the total reflector mirror through which the laser power is monitored, and A_{eff} is the effective cross-sectional area of the photolysis cell.[12,23] Thus provided T can be determined with reasonable accuracy, it is possible to confirm that the excitation rate calculated from the Stern–Volmer intercept is consistent with the absorption cross section obtained by calibration methods.

In Table I we provide a summary of the values of k_a' determined from Stern–Volmer plots and the transmittances used to convert these into absorption cross sections. The cross sections are compared with those from the methane calibration experiments. It can be seen from these data that
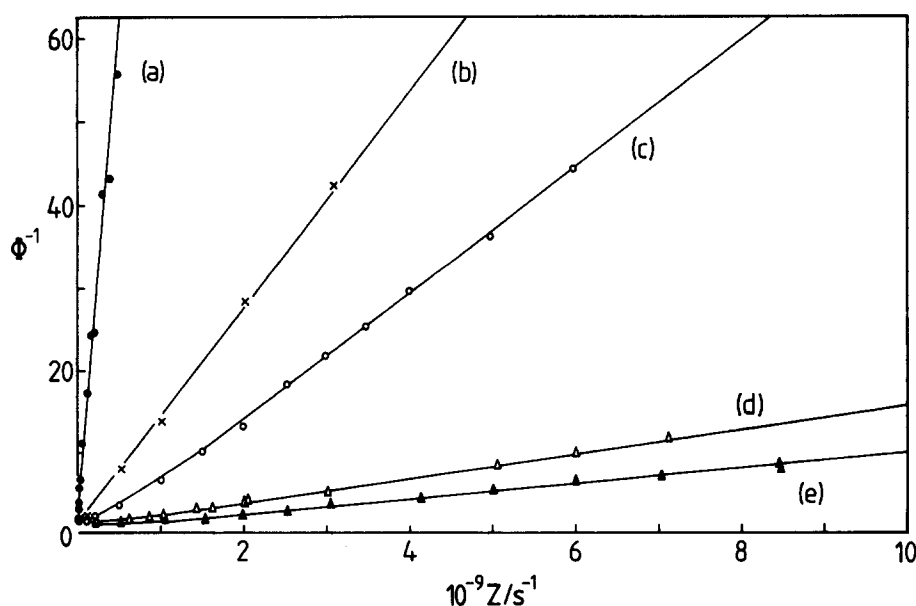

FIG. 1. Variation of reciprocal quantum yield for isomerization as a function of the frequency of collisions between excited and ground state cyclobutene. The slopes of the plots are inversely proportional to the values of $k(E*)$, and indicate a variation of almost two orders of magnitude over the energy range studied. Photolysis energies are: (a) 11 531 cm^{-1}, (b) 13 440 cm^{-1}, (c) 14 123 cm^{-1}, (d) 15 718 cm^{-1}, (e) 16 601 cm^{-1}.

TABLE I. Comparison of the cyclobutene C–H overtone absorption cross sections derived from kinetic and spectroscopic measurements.

| λ^a				Kinetic^c	Spectroscopic^d
cm^{-1}	nm	$k'_a/W^{-1}s^{-1\,b}$	T	σ/cm^2	σ/cm^2
11 531	867.2		0.021 ± 0.005		1.5×10^{-23}
13 440	744.0	0.254	$<3 \times 10^{-4}$	$<4 \times 10^{-24}$	1.9×10^{-24}
14 123	708.1	0.0297	1.14×10^{-3}	2.04×10^{-24}	2.0×10^{-24}
15 718	636.2	9.62×10^{-3}	3.74×10^{-4}	2.42×10^{-25}	2.4×10^{-25}
16 601	602.4	0.0326	1.11×10^{-4}	2.57×10^{-25}	3.2×10^{-25}

^{a} Vacuum wave numbers.
^{b} From the intercepts of plots of k_{obs}^{-1} vs pressure.
^{c} Obtained from k'_a—see the text.
^{d} From comparisons with the overtone absorption cross sections of methane and benzene—see the text.

the two *completely different* methods for determining the cross sections produced reasonably consistent results. The data for the $v = 5$ and 6 C–H overtones are generally in agreement to within a factor of 2 of the values reported by Jasinski et al.[12] For the olefinic C–H overtone at 11 531 cm^{-1} the Stern–Volmer intercept did not give a reliable estimate of the absorption cross section and so for kinetic data determined at this wavelength k'_a was calculated from the cross section obtained by the spectroscopic calibration method described above. For the higher energy overtone bands the values of k'_a listed in Table I were used to produce the reciprocal quantum yield/collision frequency plots shown in Fig. 1. The difficulties and uncertainties associated with the accurate determination of k'_a place limitations on the accuracy of the experimental reciprocal quantum yield values and hence on any parameters derived from these. We will return to this point in the Discussion section below.

Effects of different collider gases

The presence of an inert gas results in a further collisional deactivation step

$$A^*(E^*) + M \xrightarrow{Z_{AM}} A + M,$$
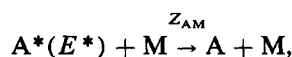
which modifies the steady-state expression, Eq. (5), giving

$$\Phi^{-1} = 1 + \frac{Z_{AA}[A] + Z_{AM}[M]}{k(E^*)}. \tag{6}$$

In experiments designed to measure collision efficiencies for different bath gases the cyclobutene pressure was maintained at a fixed value of 5 Torr and the bath gas pressure was varied from $\sim$50–1000 Torr, giving dilution ratios, expressed as $Z_{AA}[A]/(Z_{AA}[A] + Z_{AM}[M])$, of the order of 0.1 for the lowest and 0.005 for the highest bath gas pressures. With $Z_{AA}[A]$ constant, Eq. (5) indicates that the reciprocal quantum yields should vary linearly with bath gas pressure and in Fig. 2 we show the results of experiments with 15 718 cm^{-1} excitation for the collider gases SF$_6$, CHF$_3$, CO$_2$, CH$_4$, CO, N$_2$, Ar, and He. Data were also obtained for H$_2$ but are not shown in Fig. 2. In this figure, the reciprocal quantum yields are plotted against the collision frequency Z ($= Z_{AM}[M]$) with Z_{AM}, the bimolecular Lennard-Jones collision frequency, calculated according to the

procedures described below. As expected from numerous earlier studies of collisional energy transfer, the monoatomic bath gases He and Ar appear to be the least efficient and large polyatomic molecules the most efficient. We discuss below the various correlations that can be made between energy transfer efficiency and molecular parameters.

Figure 2 demonstrates the importance of the effects of weak collisions very clearly. For the gases shown, the hard-sphere collision frequencies vary only slightly and, since $k(E^*)$ is constant, the strong collision assumption would lead us to predict similar magnitudes for the slopes of the plots of reciprocal quantum yield vs collision frequency. Of course, for gases such as He and Ar the strong collision assumption is completely inappropriate; our point is that it is also inappropriate for the larger polyatomic molecules SF$_6$ and cyclobutene.

Lennard-Jones collision parameters

The bimolecular Lennard-Jones collision frequencies Z_{AM} were calculated using the standard formulas[15,24]:

$$Z_{AM} = N_A \pi \sigma_{AM}^2 \Omega_{AM}^{(2,2)*} \left(\frac{8RT}{\pi \mu_{AM}} \right)^{1/2},$$

$$\Omega_{AM}^{(2,2)} = \left[0.636 + 0.567 \log\left(\frac{k_B T}{\epsilon_{AM}} \right) \right]^{-1},$$

where σ_{AM} is the Lennard-Jones collision diameter (rather than a collision cross section), $\Omega_{AM}^{(2,2)*}$ is a reduced collision integral, and ϵ_{AM} is the Lennard-Jones well depth. All of the other symbols have their usual significance. Lennard-Jones parameters for the A–M collision partners were estimated using the combining rules

$$\sigma_{AM} = \frac{1}{2}(\sigma_A + \sigma_M),$$

$$\epsilon_{AM} = (\epsilon_A \epsilon_M)^{1/2}.$$

Where appropriate, the parameters for pure gases were obtained from the compilation of Reid and Sherwood[25] which is based on the gas viscosity data of Svehla.[26] For gases not listed in this compilation parameters were calculated from critical data using the correlation expressions developed by Steil and Thodos.[27] For cyclobutene the critical parameters were estimated using the additive rules and incremental values supplied by Reid and Sherwood,[25] and were found to be
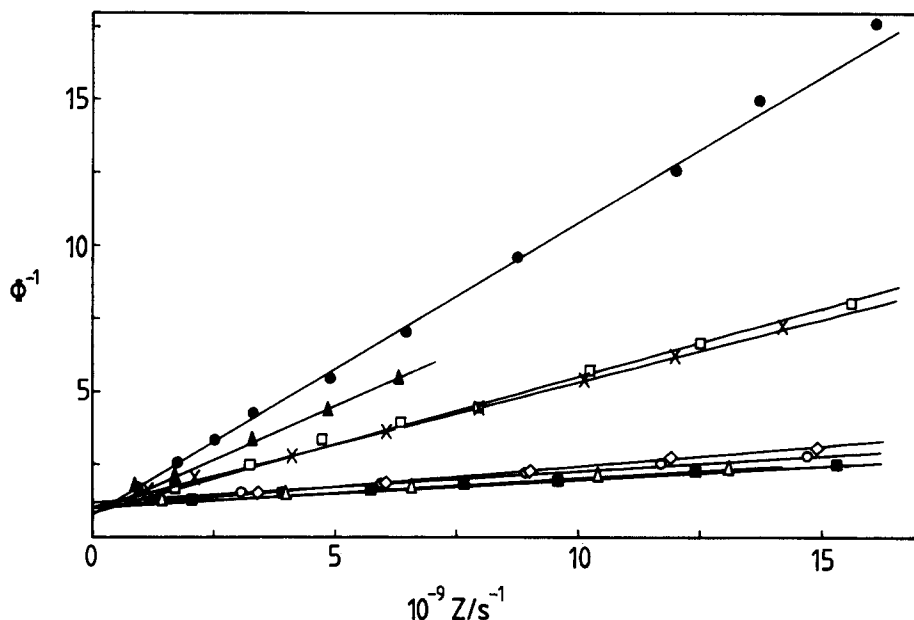
FIG. 2. Variation of reciprocal quantum yield for cyclobutene isomerization as a function of collision frequency Z ($= Z_{AM}$ [M]) in the presence of a variety of bath gases at an excitation energy of 15 718 cm^{-1}. The slopes are directly proportional to the collisional energy transfer efficiencies of the collision partners. (●) SF$_6$, (▲) CHF$_3$, (□) CO$_2$, (×) CH$_4$, (◇) CO, (○) N$_2$, (△) Ar, (■) He.

reasonably consistent with those for buta-1,3-diene and cyclopentene. The resulting estimates of σ_{AM}, ϵ_{AM}/k_B, and Z_{AM} are listed in Table II. For the gases Ar, N$_2$, CO$_2$, SF$_6$, CH$_4$, and CO, the Lennard-Jones parameters used were in good agreement with the recommended values provided in a recent evaluation by Mourits and Rummens.[28]

RRKM calculations

Estimates of $k(E^*)$ used for the determination of collision efficiencies and in master equation calculations of energy transfer step sizes were obtained using RRKM theory.[29] Densities of states of the activated molecule were calculated using the Whitten–Rabinovitch algorithm[30] and the cyclobutene fundamental frequencies reported by Baggott et al.,[31] supplemented by the Raman data of Aleksanyan and Garkusha.[32]

The activated complex frequencies were chosen to reproduce the high pressure Arrhenius A factor for cyclobutene isomerization recommended by Benson and O'Neal.[33] Many of the ground state vibration frequencies were re-

tained, with small modifications to those frequencies most obviously affected by the isomerization. These were the ring modes ν_3, ν_6, ν_7, and ν_{18} and the ring puckering vibration, ν_{13}. In one activated complex model the C–C stretch ring mode ν_7 was assigned as the reaction coordinate and ν_3, ν_6, and ν_{18} were each arbitrarily set at 1400 cm^{-1}. The ring puckering vibration was then allowed to float in order to reproduce the high pressure A factor. In a second activated complex, the ring puckering vibration was assigned as the reaction coordinate and ν_7 allowed to float. The $k(E^*)$ values computed using either model were indistinguishable except at excitation energies close to threshold, and were in good agreement with the values obtained by Elliot and Frey[34] who used a number of different grouped-frequency activated complexes. Sums of states of the activated complex were calculated using the Beyer–Swinehart algorithm as described by Stein and Rabinovitch.[35]

The first activated complex model described above was used throughout the calculations to follow. The barrier height E_0 was determined to be 11 236 cm^{-1} based on the recommended high pressure Arrhenius parameters,[33] and the results of RRKM calculations for the energy range 11 300–20 000 cm^{-1} are shown in Fig. 3. Also shown in this figure are the energies of photoactivated cyclobutene corresponding to excitation of the various C–H stretching overtones. These energies were determined as $E^* = h\nu + \langle E_{vib} \rangle$, with the average vibrational energy of ground state cyclobutene determined from the frequencies to be 249 cm^{-1} at 300 K.

Collision efficiencies

The simplest way of accounting for the effects of inefficient collisional energy transfer in a photoactivated unimolecular reaction is to introduce an efficiency parameter γ_c,[36]

$$\Phi^{-1} = \text{constant} + \frac{\gamma_c Z_{AM} [M]}{k(E^*)}.$$

TABLE II. Lennard-Jones parameters and collision frequencies.

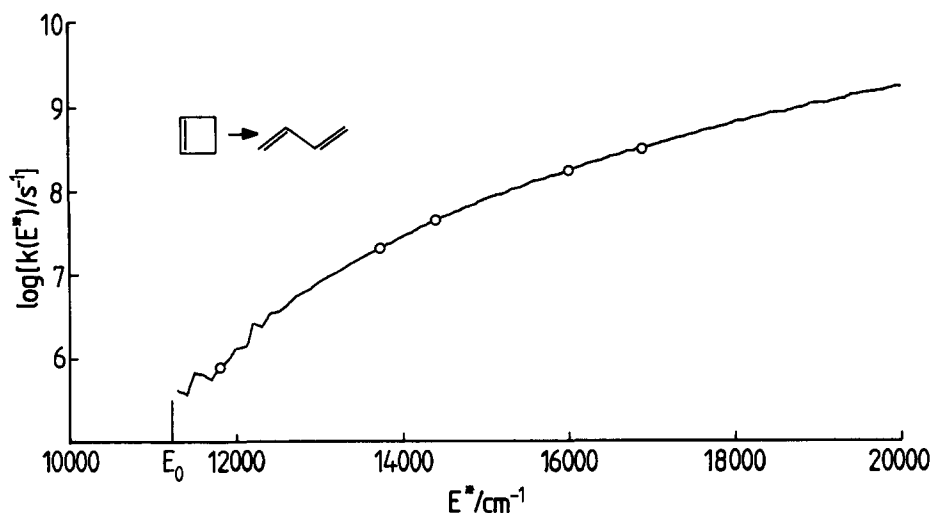| M	σ_M/Å	(ϵ_M/k_B)/K	$10^{-7} Z_{AM}$/Torr^{-1} s^{-1} [a]
Cyclobutene	5.24	250	1.99
SF$_6$	5.128	222.1	1.58
CHF$_3$	4.56	194.1	1.57
CH$_4$	3.758	148.6	1.98
CO$_2$	3.941	195.2	1.57
H$_2$	2.827	59.7	3.50
CO	3.941	91.7	1.48
N$_2$	3.798	71.4	1.46
Ar	3.542	93.3	1.29
He	2.551	10.22	1.88

[a] Cyclobutene + M collisions.

FIG. 3. Results of RRKM theory calculations for the energy-specific rate constants $k(E^*)$. The open circles indicate the energies of the cyclobutene molecules on excitation of C–H stretching overtones, computed as $h\nu + \langle E_{\mathrm{vib}} \rangle$.

Using RRKM estimates of $k(E^*)$ it is possible to obtain experimental values of the collision efficiencies directly from the slopes of the Stern–Volmer plots. These values are listed in Table III for each collider gas at the five different overtone energies studied. However, even a simple stepladder approach to collisional deexcitation shows that such efficiencies are pressure-dependent (see below), becoming independent at some high pressure limit dictated by the magnitude of $k(E^*)$: the Stern–Volmer plots are expected to show some slight nonlinearity.[36] The values listed in Table III should therefore be regarded as approximate. The collision efficiency parameters should depend in a complex fashion upon the internal energy content of the photoactivated molecule[36] and yet the values reported in Table III show little systematic dependence on the photon energy. Thus, for the purposes of comparisons with energy transfer step sizes, to be made below, average values of the γ_c's were determined and are included in Table III.

DISCUSSION

Two approaches to the treatment of inefficient collisional energy transfer in a photoactivated unimolecular reaction are available: (i) we can perform full collisional master equation calculations to deduce the values of the step sizes which provide the best fit with the experimental data typified in Figs. 1 and 2, or (ii) we can make use of the approximate relations developed by Troe[36] which are based on a simple stepladder model for energy transfer and which allow us to relate the experimental collision efficiencies to energy transfer step sizes directly. Our purpose in pursuing such analyses is to demonstrate that RRKM theory, combined with an adequate treatment of collisional energy transfer, can account satisfactorily for all of the data presented in this paper. In addition, we need to obtain estimates of energy transfer parameters so that in future experimental studies we can derive more accurate $k(E^*)$ values for comparison with RRKM theory predictions, thereby providing a more stringent test for the theory. Finally, there is the question of the energy dependence of the energy transfer parameters.

Master equation calculations

The quantum yield of a photochemical unimolecular reaction may be expressed as the ratio of the number of molecules decomposed to the total number photoexcited per unit time

TABLE III. Experimental collision efficiencies for various bath gas molecules derived from the slopes of Stern–Volmer plots.

M E^*/cm^{-1} [a]	γ_c					$\bar{\gamma}_c$
	11 780	13 689	14 372	15 967	16 850	
Cyclobutene	0.378	0.265	0.282	0.237	0.242	0.281 ± 0.057
SF_6	0.158	0.158	0.218	0.167	0.162	0.173 ± 0.026
CHF_3	0.094	0.104	0.137	0.114	0.101	0.110 ± 0.017
CH_4	0.074	0.076	0.089	0.070	0.070	0.076 ± 0.008
CO_2	0.072	0.058	0.081	0.075	0.060	0.069 ± 0.010
H_2	0.036	0.032	0.032	0.033	0.029	0.032 ± 0.003
CO	0.021	0.022	0.024	0.023	0.017	0.021 ± 0.003
N_2	0.015	0.020	0.022	0.018	0.016	0.018 ± 0.003
Ar	0.019	0.016	0.019	0.015	0.010	0.016 ± 0.004
He	0.008	0.018	0.018	0.016	0.007	0.013 ± 0.005

[a] $E^* = h\nu + <E_{\mathrm{vib}}>$.

$$\Phi = \frac{D}{S+D} ; \quad \Phi^{-1} = 1 + \frac{S}{D}.$$

Here D is the number of molecules decomposed and S is the number of molecules stabilised by collisions. We have taken the S/D ratios obtained from our experimental studies of cyclobutene isomerisation induced by overtone excitation and used them in a collisional master equation analysis to find the values of the energy transfer step sizes $\langle \Delta E \rangle$. The master equation approach has been in use for many years and may be implemented in a number of different ways.[37–44]

In our calculations the excited molecules were first created with an energy distribution equivalent to the room temperature vibrational energy distribution displaced by the photon energy[44] (calculations in which a delta-function excitation at $h\nu + \langle E_{\text{vib}} \rangle$ was assumed gave very similar results). This initial distribution was then subjected to a sequence of collisions with a fixed energy transfer step size which resulted in the distribution spreading on a ladder of quasiquantized energy levels and tending downwards towards the threshold of unimolecular reaction (see, for example, Figs. 2–5 of Ref. 42 and Figs. 1 and 2 of Ref. 44). At each collision the numbers of molecules reacted and stabilized were accumulated. Rate constants for unimolecular reaction at specific energies within the distribution were calculated using RRKM theory in the manner described above. The process was repeated iteratively until the value of $S + D$ was unity.[39]

At each collision, the excited molecules may lose or gain energy depending on the form of the step size distribution function $P(E,E')$, where E is the energy of the molecule prior to collision and E' is the energy following the collision. The exact form of $P(E,E')$ is not known and it is usual to assume some arbitrary function. In all of our master equation calculations described in the present paper we have used the exponential-down model

$$P_d(E,E') = \frac{1}{N(E)} \exp[-(E-E')/\alpha],$$

where $P_d(E,E')$ represents the probability of collisional removal of energy from the excited molecule $E' < E$ and $N(E)$ is a normalization constant. We take the step size parameter α to be related to the average energy transferred in a down step according to the expression $\alpha = -\langle \Delta E \rangle_d$. The probability that the excited molecule may gain energy via collisions is obtained by detailed balance:

$$P_u(E,E') = \frac{\rho(E')}{\rho(E)} P_d(E',E) \exp[-(E'-E)/k_B T],$$

where $\rho(E)$ is the vibrational state density at the energy E and $E' > E$. In practice, for a given initial energy distribution, the magnitude of $\langle \Delta E \rangle_d$ was varied and the corresponding S/D ratios calculated as a function of the total pressure. Where applicable, full account was taken of the relative probabilities for collisions involving inert bath gas molecules and ground state cyclobutene. The values of $\langle \Delta E \rangle_d$ which produced the best agreement between calculated and experimental S/D ratios for a given photon energy and collider gas were thus determined.

The exponential-down model favors small steps and is thought to be the most appropriate for very inefficient ener-

gy transfer. In a preliminary communication[17] which described the results of experiments performed on cyclobutene excited at 16 601 cm^{-1}, corresponding to the $v = 6$ overtone of the olefinic C–H stretch, both the exponential-down and stepladder models were employed. Calculations demonstrated that although very different values result for $\langle \Delta E \rangle_d$, both models predict similar values for the average energy transferred $\langle \Delta E \rangle$, which includes all up and down transitions. In recovering average $\langle \Delta E \rangle$ values from $\langle \Delta E \rangle_d$ we have used the expression derived by Barker and Golden[45]

$$\langle \Delta E \rangle = \left[\frac{1}{\langle \Delta E \rangle_d} + \frac{1}{k_B T} + \frac{s-1}{E + aE_Z} \right]^{-1} - \langle \Delta E \rangle_d$$

in which s is the number of vibrational modes, E_z is the zero point energy, and a is an empirical parameter which varies with energy. This expression represents an improvement on the approximate relationship used by Troe and co-workers[15] in that it takes some account of the variation of vibrational state density with energy but which in fact produced only minor differences in the $\langle \Delta E \rangle$ values. Tardy and Rabinovitch have given a recent critique of the various approaches to the determination of average energy transfer quantities in the exponential model.[46] The resulting best-fit values for the average step sizes $\langle \Delta E \rangle$ are shown in Table IV. Standard deviations for the $\langle \Delta E \rangle$'s have been estimated from the single standard deviations of the intercepts of the plots of k_{obs}^{-1} vs pressure and therefore reflect the uncertainties in the experimental rate constants.

Absolute magnitudes of the $\langle \Delta E \rangle$ values

Some of the most recent estimates of energy transfer step sizes involving large vibrationally excited polyatomic molecules come from the time resolved studies of Rossi et al.[14] and of Hippler et al.[15,47] Controversy surrounds the findings of Rossi et al. which seemed to indicate that the step sizes for all collider gases approximately doubled in magnitude when the internal vibrational energy content of excited azulene was increased from 17 500 to 30 600 cm^{-1}. These experiments were based on the observation of the decay of IR emission from C–H stretch fundamentals which was used as a direct monitor of the internal energy of the vibrationally excited molecule. In a more recent study, Hippler et al.[47] monitored the time-resolved UV absorption of vibrationally excited azulene at an initial internal energy of 30 600 cm^{-1} but for nonpolar collider molecules observed considerably less variation in the step sizes over the energy range in question. A calibration problem was suggested[47] to be the explanation for this discrepancy. However, over the energy range pertinent to the present study, ~ 12 000–17 000 cm^{-1}, all colliders showed some small dependence on energy.

The magnitudes of the energy transfer step sizes reported in Table IV are consistently smaller than the values obtained in the recent direct studies of Hippler et al.[15,47] For the strong colliders cyclobutene and SF$_6$ our determinations of $\langle \Delta E \rangle$ vary somewhat haphazardly with energy but are generally some 150–200 cm^{-1} smaller than the values expected for a C$_4$ hydrocarbon and SF$_6$ based on direct measurements.[14,15,47] We do not believe that such a discrepancy is particularly serious given the uncertainties inherent in any

TABLE IV. Energy transfer parameters obtained from numerical solution of the collisional master equation.

M	$E*/\text{cm}^{-1}$ [a]	$-\langle\Delta E\rangle/\text{cm}^{-1}$ [b]					$-\overline{\langle\Delta E\rangle}/\text{cm}^{-1}$ [c]
		11 780	13 689	14 372	15 967	16 850	
Cyclobutene		408 ± 70	323 ± 28	368 ± 44	378 ± 14	444 ± 57	384 ± 45
SF_6		198 ± 25	222 ± 23	323 ± 45	283 ± 10	308 ± 42	267 ± 54
CHF_3		108 ± 13	130 ± 13	184 ± 25	191 ± 9	209 ± 34	164 ± 43
CH_4		80 ± 9	91 ± 9	114 ± 15	112 ± 6	133 ± 21	106 ± 21
CO_2		71 ± 8	73 ± 7	94 ± 13	116 ± 5	112 ± 17	93 ± 21
H_2		35 ± 4	36 ± 3	38 ± 5	49 ± 2	50 ± 7	42 ± 7
CO		18 ± 3	24 ± 3	20 ± 5	35 ± 2	42 ± 9	28 ± 10
N_2		16 ± 2	23 ± 3	17 ± 4	32 ± 2	41 ± 9	26 ± 11
Ar		10 ± 2	18 ± 2	24 ± 4	25 ± 1	29 ± 7	21 ± 7
He		7 ± 1	20 ± 2	22 ± 3	27 ± 2	28 ± 8	21 ± 8

[a] $E* = h\nu + \langle E_{vib}\rangle$.
[b] Single standard deviations estimated from the errors associated with the intercepts of the Stern–Volmer plots of k_{obs}^{-1} vs pressure.
[c] Unweighted average; single standard deviation.

measurement of intermolecular energy transfer. Indeed, in their work on azulene, Hippler et al.[47] comment on the uniformity of $\langle\Delta E\rangle$ values determined for vibrationally excited toluene and azulene, and yet the data provided in Table II of Ref. 47 shows that for many of the inert collider gases $\langle\Delta E\rangle$ for collisions with excited azulene are larger by several hundred cm^{-1}. Given that the magnitudes of the energy transfer parameters will depend on the nature of the intermolecular potential surfaces, the details of which we are largely ignorant, we may regard the step sizes determined in the present work for the strong colliders to be at least consistent with previous studies and to justify our approach. However, for the weak colliders He, Ar, N_2, and CO our studies indicate extremely small energy transfer step sizes and we must therefore examine our experiments closely to discover if these values are accurately reflecting the abilities of the atomic and diatomic colliders to remove energy from vibrationally excited cyclobutene. It should be emphasised that our determinations of $\langle\Delta E\rangle$ for these weak colliders are not being distorted by curvature in the Stern–Volmer plots. Such curvature is indeed predicted by our model but, taking the example of He collider gas at an excitation energy of 15 718 cm^{-1} (cf. Fig. 2), no deviation from linearity is indicated above pressures of ~ 25 Torr, corresponding to collision frequencies of $0.47 \times 10^9 \text{ s}^{-1}$. Extension of the calculation to very high pressures ($\sim 10\,000$ Torr) shows that no further curvature is expected.

Our determinations of $\langle\Delta E\rangle$ depend ultimately on the accuracy of the RRKM estimates of $k(E*)$ and hence on the accuracy of the high pressure unimolecular rate data used to fix the activated complex frequencies and the barrier height. A reduction of the barrier height by as little as 100 cm^{-1} can lead to significantly increased values for $\langle\Delta E\rangle$. However, it would be quite wrong to introduce arbitrary reductions in the barrier height (equivalent to reducing the activation energy) without simultaneously reducing the value of the A factor, since the values of the high pressure rate constants for thermal isomerization of cyclobutene are very well determined. If these parameters are changed in an equivalent direction simultaneously the resulting effect on the shape of

the $k(E*)$ curve is minimal. We have made the further assumption in our RRKM calculations that the magnitudes of the energy-specific rate constants are not affected by rotational motion of the reactant; i.e., we have not performed a full $k(E,J)$ calculation and the ratio of rotational partition functions of the activated complex and reactant molecule has been set to unity. We justify this assumption by noting that the high pressure A factor is not unusually large, as would be expected of a unimolecular reaction in which rotational excitation plays an important role.[29]

The magnitudes of the bimolecular Lennard-Jones collision frequencies will dictate the number of collisions suffered by the activated cyclobutene in competition with unimolecular reaction and thus the values of the step sizes obtained. In calculating the collision frequencies we have followed the recognized procedures used by other authors and which should ensure comparability between energy transfer step sizes determined by any technique. However, we are obviously making the assumption, without justification, that we can identify the Lennard-Jones collision diameters and well depths for the vibrationally excited cyclobutene with those of the ground state molecule and that the collision frequencies are independent of energy.

Our vibrationally excited reactant molecule has fewer vibrational degrees of freedom than the molecules studied recently by direct methods. In the ergodic collision theory of Nordholm et al.[48] a simple relationship was developed which indicated a direct connection between $\langle\Delta E\rangle$ and the number of vibrational modes of both the excited molecule and collider. However, $\langle\Delta E\rangle$ was deduced to depend inversely on the number of vibrational modes of the excited molecule and would lead us to expect slightly larger energy transfer step sizes for cyclobutene compared to toluene and azulene in contrast to our observations.

Smaller energy transfer step sizes imply that the reaction is more difficult to quench than expected. If we were to adopt the parameters determined recently by Hippler et al.[15,47] as being applicable to vibrationally excited cyclobutene we would necessarily obtain $k(E*)$ values larger than predicted by RRKM theory. Such a discrepancy would arise

if some additional photochemical channel leading to isomerization were present. Examples include rapid reaction from an electronically excited state which might be present as a weak continuum absorption underneath the overtone transitions and which would not necessarily be detected by photoacoustic techniques or localized heating of the cyclobutene in the region of the reaction cell windows due to the presence of high intensity radiation.[9] We can dismiss both of these possibilities since, as described earlier, the presence of high intensity radiation not resonant with an overtone transition produced no observable isomerization on timescales typical of our measurements.

We have already voiced reservations about our ability to determine accurate values for the excitation rate constants k'_a. Clearly, use of k'_a values larger than those reported in Table I might resolve any discrepancy between the energy transfer step sizes simply by increasing the number of excited molecules produced and hence the experimental S/D ratios. The larger the S/D ratio at a given excitation energy, the larger the energy transfer step size required to reproduce the data. However, the agreement obtained between the overtone absorption cross sections determined from Stern–Volmer intercepts and from spectroscopic calibrations given in Table I seems to indicate that the values of k'_a used in the calculations are reasonable. Indeed, for the data at 11 531 cm^{-1}, where we were forced to use the absorption cross section determined by the spectroscopic calibration method to calculate k'_a, the resulting energy transfer step sizes are of a similar order of magnitude to the values obtained at higher photon energies. There remains the question of the accuracy of a spectroscopic calibration technique based on the comparison of peak absorption cross sections derived from measurements at different resolution.

In the above arguments there is no single factor which might be expected to influence the energy transfer step sizes of some collider molecules more than others and so we must conclude that our determinations of the relative collision efficiencies, as shown in Fig. 2 and Tables III and IV, are accurate. If we accept that the step sizes associated with the strong colliders cyclobutene and SF$_6$ are resonable, then we must also accept that the step sizes obtained for the atomic and diatomic colliders do reflect correctly their energy transfer efficiencies.

Variation of $\langle\Delta E\rangle$ values with E

For each bath gas studied the energy transfer step sizes obtained from numerical solution of the collisional master equation show a general decrease with decreasing excitation energy. Although the trend is not particularly well defined because of the large uncertainties associated with each individual measurement of $\langle\Delta E\rangle$, the energy dependences can be seen to be relatively small. For example, for SF$_6$ the value of $\langle\Delta E\rangle$ increases from 198 to 308 cm^{-1} over an energy range spanning 5070 cm^{-1}. This may be viewed either as a proportional increase of $\sim 36\%$ or as an absolute increase of 110 cm^{-1}. Such absolute changes are shown in Fig. 4 for a selection of the bath gas molecules in terms of plots of $\langle\Delta E(11\ 780)\rangle - \langle\Delta E(E^*)\rangle$ vs E^*. This figure shows that the absolute increases are greatest for SF$_6$, becoming pro-
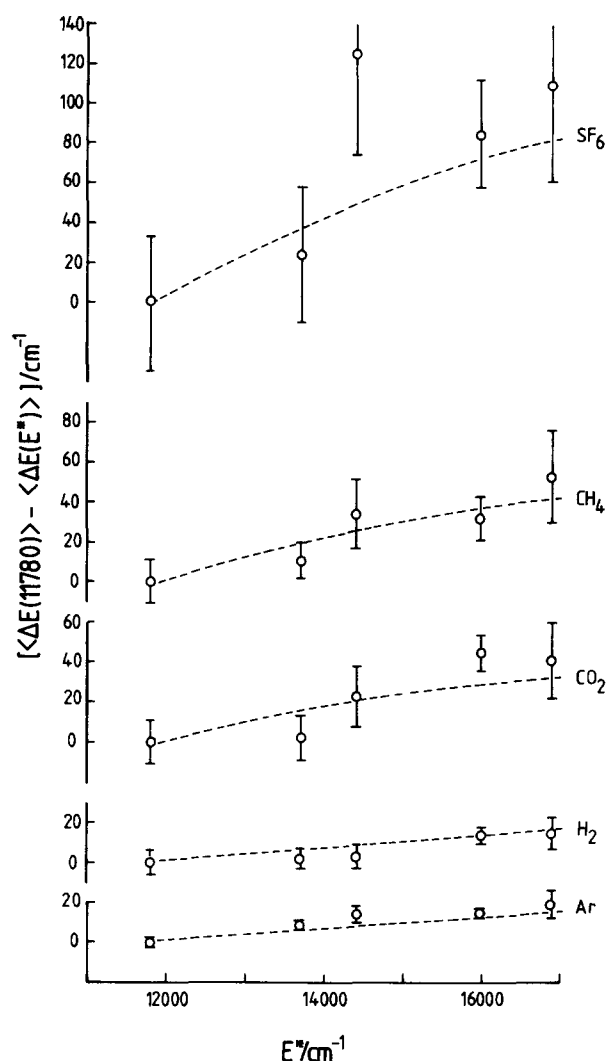

FIG. 4. Variation of the collisional energy transfer step sizes as a function of the excitation energy expressed in terms of absolute increases in $-\langle\Delta E(E^*)\rangle$ above the value determined at 11 780 cm^{-1}. Also shown as the dashed lines are the equivalent variations obtained from the data of Hippler et al., Ref. 47.

gressively smaller for the weaker colliders. Also plotted in this figure as the dashed lines are similar dependences derived from the data of Hippler et al.[47] for collisional deactivation of vibrationally excited azulene. The comparison is a striking one, although it must be remembered that we are deducing absolute rather than proportional changes. Thus, our data would be approximately reproduced if we were to displace the $\langle\Delta E\rangle$ vs $\langle E\rangle$ curves determined by Hippler et al.[47] such that the $\langle\Delta E\rangle$ values at $E^* = \langle E\rangle = 11\ 780$ cm^{-1} were in agreement. Alternatively, given a value of $\langle\Delta E(11\ 780)\rangle$ for a particular collider molecule we could, in principle, use the data of Hippler et al. to determine the absolute increase in $\langle\Delta E\rangle$ expected over a 5000 cm^{-1} interval.

If the comparisons made in Fig. 4 are legitimate, they would seem to indicate that the form of the dependence of $\langle\Delta E\rangle$ upon energy is determined largely by the collider molecule, the nature of the vibrationally excited collision partner determining only the relative magnitude of $\langle\Delta E\rangle$,

i.e., determining the vertical displacement of the $\langle \Delta E \rangle$ vs energy curve. If we accept that the comparisons made in Fig. 4 are meaningful, then we may conclude that the energy dependences of $\langle \Delta E \rangle$ for collisions of inert bath gas molecules with vibrationally excited cyclobutene are consistent with the recent determinations of Hippler et al.[47] and point to relatively weak variations.

Correlation of $\langle \Delta E \rangle$ with molecular parameters

Figure 4 and the discussion above illustrate that the $\langle \Delta E \rangle$ values are only weakly dependent on the amount of initial excitation energy. Thus, in order to develop various correlations of the $\langle \Delta E \rangle$'s with molecular parameters we have determined mean values for the step sizes $\langle \overline{\Delta E} \rangle$, which are included in Table IV.

In Fig. 5 we show four different ways of comparing the mean step sizes with various parameters of the collider molecules. With the exception of the plot of $\langle \overline{\Delta E} \rangle$ vs T_b, which is somewhat scattered, these correlations show the forms expected from many previous studies of intermolecular energy transfer in both thermal and photochemical systems. The most satisfactory of these is the correlation between $\langle \overline{\Delta E} \rangle$ and N, the number of atoms in the bath gas molecule, which has been noted by other authors as providing one of the best

methods of relating the step size to the specific collider. Figure 5 gives us confidence that we are able to distinguish effects of weak intermolecular energy transfer in our kinetic data.

Approximate treatments

The data of Tables III and IV indicate that we might expect to find a correlation between mean step size and the experimental collision efficiency γ_c. These parameters are plotted in Fig. 6 which demonstrates an approximately linear relationship. That these parameters should be highly correlated should come as no surprise since the same reciprocal quantum yield data has been used in their determination and we have also introduced some averaging. Figure 6 indicates that it should be possible to find an approximate treatment of collisional energy transfer which can be used to relate $\langle \overline{\Delta E} \rangle$ to γ_c, allowing us to estimate $\langle \overline{\Delta E} \rangle$ directly from the slopes of the Stern–Volmer plots without recourse to numerical solution of the master equation. Such an approximate treatment has been developed by Troe[36] and we give some attention here to the details of that development.

The simplest stochastic model that may be used to treat collisional energy transfer is the stepladder model, which views the transfer process in terms of removal of energy in
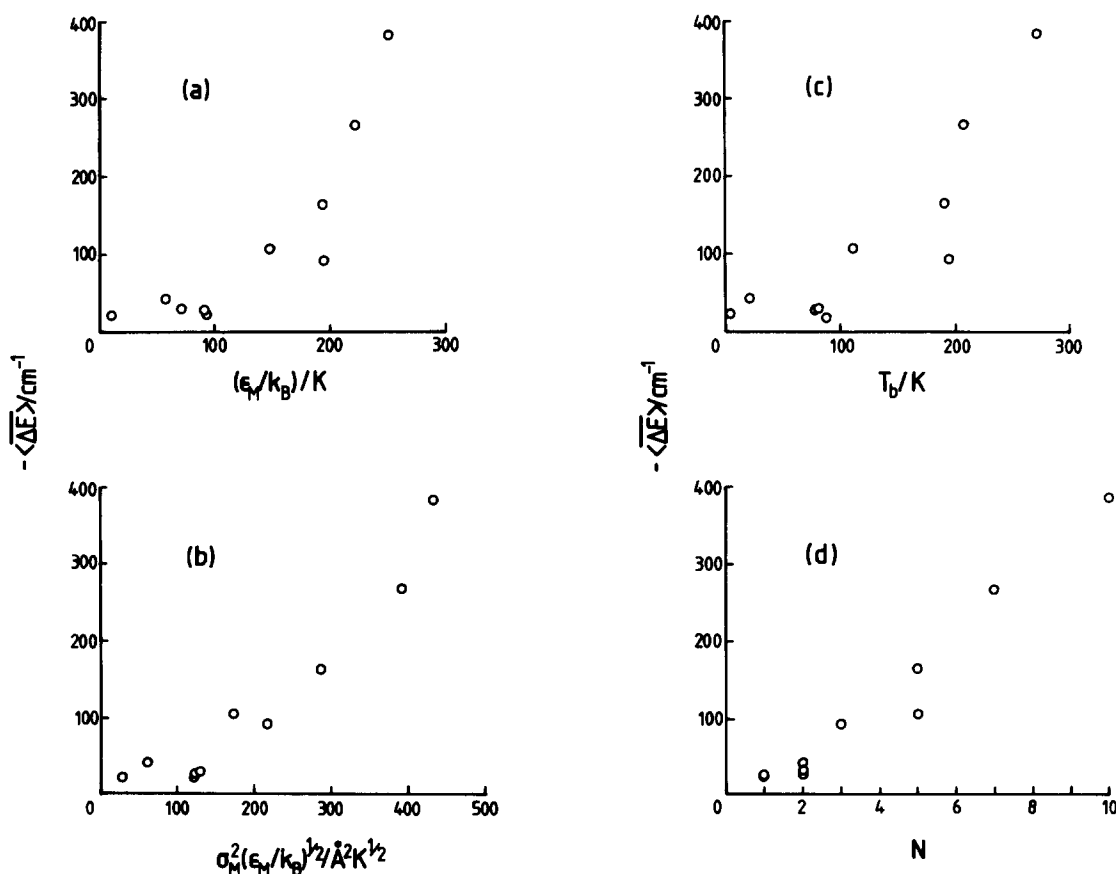

FIG. 5. Correlation diagrams relating the mean energy transfer step sizes to various molecular properties of the collider gases. (a) Lennard-Jones well depth ϵ_M/k_B; (b) $\sigma_M^2 \epsilon_M^{1/2}$; (c) boiling temperature T_b; (d) number of atoms N.
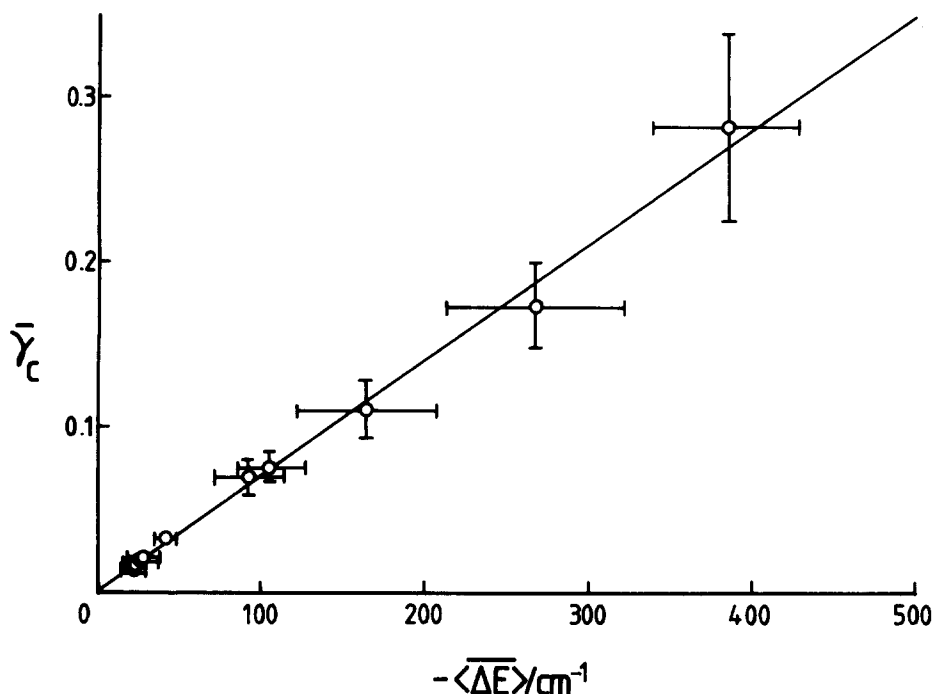
FIG. 6. Correlation of the mean collision efficiency parameters with mean energy transfer step size.

fixed steps on each collision. The model is illustrated in Fig. 7 which refers to the situation obtained for cyclobutene excited at 16 601 cm^{-1}. In this case, many steps are required to deactivate the excited cyclobutene to a level which is below the threshold for unimolecular reaction, and at each step in the sequence above E_0 reaction may proceed at a rate determined by the value of $k(E^*)$. At each energy level E_i^* the probability that the molecule experiences a deactivation step rather than reaction is given by the quantity $Z/[Z + k(E_i^*)]$, where $Z = Z_{AM}[M]$. The probability of collisional stabilization is, therefore[37]

$$\frac{S}{S+D} = \prod_{i=1}^{T}\left[\frac{Z}{Z + k(E_i^*)}\right],$$

where T denotes the number of steps (collisions) required to reduce to energy of the excited molecule below E_0. In this simple model the energy distribution is "contracted" at each step and is thus not allowed to spread among the available energy levels. The stepladder calculations reported in a preliminary paper[17] differ in this regard since both up and down transitions were allowed resulting in a spreading of the distribution as a function of the number of collisions. The step size which may be deduced by application of the simple stepladder scheme is therefore a closer approximation to $\langle\Delta E\rangle$ than to $\langle\Delta E\rangle_d$. Recalling that $S/D = \gamma_c Z/k(E_{ac}^*)$, where E_{ac}^* is the initial excitation energy, we may write

$$\gamma_c = \frac{k(E_{ac}^*)}{Z\left\{\left(\frac{1}{Z}\right)^T\prod_{i=1}^{T}[Z + k(E_i^*)] - 1\right\}}, \tag{7}$$

which demonstrates that the collision efficiency parameter is expected to be pressure dependent. In the limit of very high pressure, $Z \gg k(E_i^*)$ and γ_c may be approximated as[37]

$$\gamma_c \simeq \frac{k(E_{ac}^*)}{\Sigma_{i=1}^{T}\ k(E_i^*)}, \tag{8}$$

i.e., γ_c becomes independent of pressure with a value which will depend in a very specific way on the amount of excitation energy. This treatment may be developed further[36] by approximating the sum in Eq. (8) as an integral and using a simple empirical expression to relate the $k(E_i^*)$ values to the energy. However, these approximations are likely to break down in the present situation where the reaction is studied at energies very close to threshold. Nevertheless, we can make use of Eq. (7) in numerical solutions by adjusting the magnitude of the step size to reproduce the experimental S/D ratios. This has been done for the example shown in Fig. 7, which corresponds to the data obtained for pure cyclobutene at an excitation energy of 16 601 cm^{-1} and for which a step size of 410 cm^{-1} was found to be appropriate. This value can be seen to be within the experimental error of value deduced for $-\langle\Delta E\rangle$ using the exponential-down model in the full collisional master equation treatment. The advantage of the simple analysis is that, with algorithms or machine code routines for evaluating sums of states, $\langle\Delta E\rangle$ values may be determined from experimental data with the aid of a desktop microcomputer.

However, while the simple model appears to provide an adequate treatment of the collisional energy transfer problem at energies high above threshold, the model predicts a strong dependence of $\langle\Delta E\rangle$ on energy as threshold is approached, such that the $\langle\Delta E\rangle$ values obtained for an excitation energy of 11 531 cm^{-1} are very much smaller than those determined from the full master equation calculations. This is almost certainly due to the neglect of the spreading of the distribution which becomes progressively more critical close
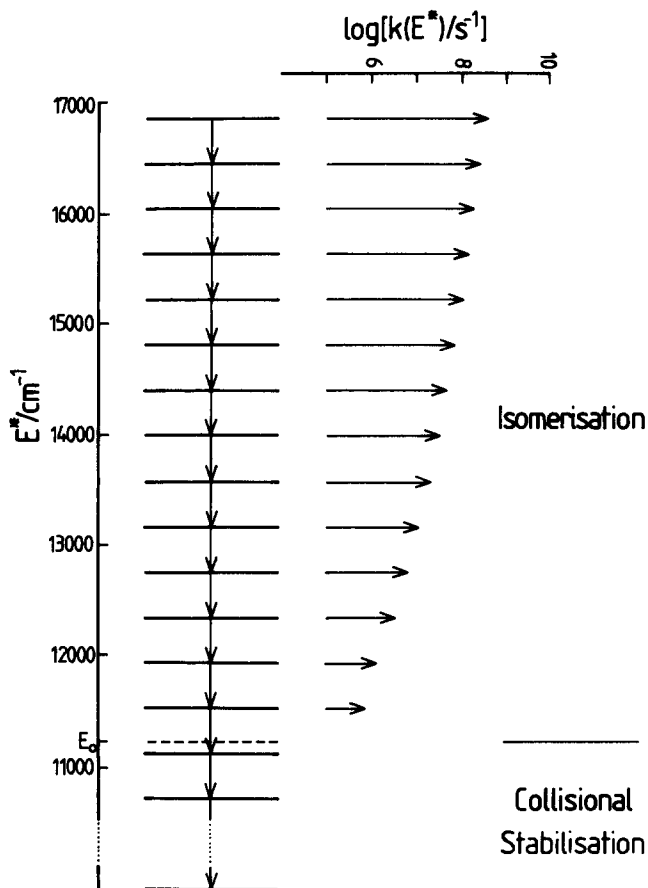
FIG. 7. The simple stepladder approach to collisional energy transfer, illustrated for the case of cyclobutene excited at 16 601 cm^{-1} with a step size of 410 cm^{-1}, the value found to reproduce the experimental quantum yields.

through coupling with other vibrational modes: a subpicosecond timescale is indicated for the methylenic C–H stretch overtones.[12] Recent theoretical studies of the dynamics of overtone excitation suggest that a quantum tunneling description is appropriate,[49] with the result that IVR within a polyatomic molecule occurs much faster than the excitation process. In the present paper, we have not questioned the validity of the statistical assumption and, in fact, Hase[50] has noted that the observation of RRKM behavior in kinetic data derived from steady-state measurements such as ours may not be particularly well suited to this problem.

If RRKM theory is indeed valid in the present application, as seems likely, the small discrepancies observed by Jasinski et al.[13] between experimental and calculated $k(E^*)$ values is readily explained in terms of inefficient collisional energy transfer by unexcited cyclobutene. Jasinski et al.[13] reconciled their results with the predictions of RRKM theory by keeping to a strong collision assumption and introducing small changes in the activated complex frequencies. However, such changes destroyed the agreement between the chosen model and the high pressure thermal rate data.

The intermolecular energy transfer parameters determined in the present work from numerical solutions of the collisional master equation appear to be internally self-consistent; i.e., a pattern of relative efficiencies is established which, with some minor exceptions, agrees well with previous studies. However, the experimental values of $\langle \Delta E \rangle$ are very small, a feature for which we are able to produce no adequate explanation. Arguments have been presented to reinforce the general conclusion that the $\langle \Delta E \rangle$'s have not been distorted by some unreasonable bias either in the experimental data or in the calculations. A small dependence of the $\langle \Delta E \rangle$ values on excitation energy has been noted, which, when expressed in absolute terms, compares favorably with recent direct studies of Hippler et al.[47]

to threshold. In the original development of Troe,[36] he applied such an approximate treatment to quantum yields obtained for the isomerization of highly vibrationally excited toluene at energies well above threshold where such problems are less important.

For the purposes of future work which might require prior knowledge of $\langle \Delta E \rangle$ or γ_c to allow $k(E^*)$ values to be determined for comparison with RRKM predictions in unimolecular reactions induced by overtone excitation, the data of Fig. 6 may be used directly.

CONCLUDING REMARKS

Intermolecular energy transfer parameters have been derived from studies of the unimolecular isomerization of gas phase cyclobutene induced by excitation of C–H stretching overtone states. RRKM theory has been assumed, with the activated complex frequencies and barrier height fixed by reference to high pressure thermal rate data. The use of RRKM theory is this fashion assumes rapid redistribution of initial excitation energy implicitly. Previous studies of the cyclobutene overtone spectra[12] indicate that, given that a pure local mode vibration may be prepared (unlikely in the present experiments) it will rapidly lose its local character

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