

# Relaxation within and from the $(3_1/2_1 4_1 5_1)$ and $(3_1 4_1/2_1 4_2 5_1)$ Fermi dyads in acetylene: Vibrational energy transfer in collisions with $C_2H_2$ , $N_2$ and $H_2$ †

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Infrared-ultraviolet double resonance (IRUVDR) experiments have been performed on samples of pure  $C_2H_2$  and on  $C_2H_2$  diluted in  $N_2$  and  $H_2$ . Pulses of tunable IR radiation from an optical parametric oscillator (OPO) excited molecules of  $C_2H_2$  to one component state of one of two Fermi dyads in the  $\tilde{X}^1\Sigma_g^+$  electronic ground state, i.e.  $(3_1/2_1 4_1 5_1)_{II}$  or  $(3_1 4_1/2_1 4_2 5_1)_{II}$ , and tunable UV laser radiation was used to observe the evolution of population either in that state or in the other component state of the same Fermi dyad. In this paper,‡ rate coefficients are reported for two kinds of processes: (a) vibration-to-vibration (V–V) transfer between the two component states of the same Fermi dyad induced by collisions with  $C_2H_2$ ,  $N_2$  and  $H_2$ , and (b) vibrational relaxation from the coupled pair of Fermi dyad states in collisions with the same gases. In addition, populations have been observed in the  $(4_2 5_1)$ ,  $(4_1 5_1)$  and  $(4_2)$  states of  $C_2H_2$  during relaxation from the  $(3_1 4_1/2_1 4_2 5_1)$  dyad and rate coefficients for self-relaxation from the first two of these states have been derived. The results for both V–V intradyad transfer and for vibrational relaxation are discussed in terms of the vibrational matrix elements for such collision-induced transitions and differences in the mixing of the zero order states in the Fermi dyads.

The spectroscopy and dynamics of acetylene provide a valuable bridge between the properties of two limiting classes of molecules. On the one hand are diatomic molecules, which are characterised by discrete and well-separated rovibrational levels. In this case, unimolecular, intra-molecular vibrational redistribution is non-existent and collisionally induced vibrational relaxation is generally inefficient.<sup>1</sup> At the other extreme are large polyatomic molecules. Except at the very lowest levels of excitation, they have a high density of rovibrational levels which cannot be described in terms of any simple, normal mode basis. Intramolecular vibrational redistribution is generally very rapid and collisionally induced energy transfer is usually facile.<sup>2</sup> Over the past few years, recognition of these factors has led to a rather large number of detailed spectroscopic<sup>3–12</sup> and dynamical<sup>8–12</sup> studies of isolated acetylene in its  $\tilde{X}^1\Sigma_g^+$  electronic ground state, as well as numerous investigations of collisionally induced transfer between the rovibrational levels of this state.<sup>13–32</sup>

In the context of the present experiments, which examine collisionally induced processes in  $C_2H_2$  involving vibrational levels that exhibit a high degree of mixing between zero order normal modes, it is useful to review briefly some of the spectroscopic properties of  $C_2H_2(\tilde{X}^1\Sigma_g^+)$ . In this electronic state,

$C_2H_2$  is linear and possesses five normal mode vibrations: three stretching modes  $\nu_1$  ( $\sigma_g^+$  symmetry, C–H symmetric stretch),  $\nu_2$  ( $\sigma_g^+$  symmetry, C–C stretch), and  $\nu_3$  ( $\sigma_u^+$  symmetry, C–H asymmetric stretch), and two doubly degenerate bending modes  $\nu_4$  ( $\pi_g$  symmetry, the *trans*-bend) and  $\nu_5$  ( $\pi_u$  symmetry, the *cis*-bend). At this level, the only infrared active fundamental transitions are those associated with the  $\nu_3$  and  $\nu_5$  modes.

In practice, however, extensive studies of the rovibrational spectrum of  $C_2H_2$  (for example, ref. 3–9, and references therein) and of the dispersed fluorescence and stimulated emission pumping spectra from the  $\tilde{A}^1A_u$  electronically excited state (for example, ref. 9–12, and references therein), involving levels with vibrational term values up to *ca.* 18,500  $cm^{-1}$ , reveal the shortcomings of a normal mode description of the vibrational levels in  $C_2H_2(\tilde{X}^1\Sigma_g^+)$ . In particular, there are strong Fermi resonances, such as that generated by the anharmonic constant  $K_{2345}$ , even at the lowest level at which this becomes possible. Such is the strength of these interactions, that a polyad or ‘cluster’ model<sup>33</sup> has been used<sup>5,9–12</sup> to describe the vibrational levels of  $C_2H_2(\tilde{X}^1\Sigma_g^+)$ . In this approach, the normal vibration quantum numbers are discarded in favour of three new quantum numbers:

$$n_s = \nu_1 + \nu_2 + \nu_3 \quad (1a)$$

$$n_r = 5\nu_1 + 3\nu_2 + 5\nu_3 + \nu_4 + \nu_5 \quad \text{and} \quad (1b)$$

$$k = l_4 + l_5 \quad (1c)$$

where  $\nu_i$  is the vibrational quantum number associated with the *i*th normal mode and  $l_4$  and  $l_5$  are the quantum numbers for the vibrational angular momenta associated with the  $\nu_4$  and  $\nu_5$  bending modes. As already mentioned, this strong coupling is evident at even the lowest level of excitation, the Fermi resonance between the *ungerade* ( $\sigma_u^+$ ) zero order states (00100), here referred to as  $3_1$ , and [010(11)<sup>0</sup>], i.e.  $2_1(4_1 5_1)^0$ , being so strong that the wavefunctions for the two vibrational

† In this paper, we employ the notation for vibrational states whereby, for example,  $3_1$  denotes one quantum of excitation in the  $\nu_3$  normal mode. thus  $(3_1/2_1 4_1 5_1)_{I,II}$  denotes the Fermi dyad in which the principal contributions to the vibrational eigenstates are from the normal mode wavefunctions describing the zeroth-order  $3_1$  fundamental and  $2_1 4_1 5_1$  combination vibrational states. In each dyad, the subscript II is used to denote the lower of the two component states, I the higher.

‡ The succeeding paper, referred to hereafter as Part II, describes measurements on the rate coefficients for transfer, between specific rotational levels within state II of the  $(3_1/2_1 4_1 5_1)$  dyad in collisions of  $C_2H_2$  with  $C_2H_2$ , Ar, He and  $H_2$ , and on the rates of transfer from the  $J = 10$  level of  $(3_1/2_1 4_1 5_1)_{II}$  to specific J levels in  $(3_1/2_1 4_1 5_1)_I$  in collisions with  $C_2H_2$ .

**Table 1** Spectroscopic parameters for the Fermi dyads derived from the  $3_1$  and  $2_14_15_1$  and from the  $3_14_1$  and  $2_14_25_1$  zero order states

	$\nu_0/\text{cm}^{-1}$ <sup>a</sup>	Wavefunctions as linear combinations of zero order basis functions <sup>b</sup>
$(3_14_1/2_14_25_1)_I$	3898.34	$0.688  3_14_1^1\rangle + 0.625  2_14_2^25_1^{-1}\rangle + 0.367  2_14_2^05_1^1\rangle + \dots$
$(3_14_1/2_14_25_1)_{II}$	3882.41	$0.723  3_14_1^1\rangle - 0.632  2_14_2^25_1^{-1}\rangle - 0.279  2_14_2^05_1^1\rangle + \dots$
$(3_1/2_14_15_1)_I$	3294.84	$0.718  3_1\rangle + 0.696  2_14_15_1\rangle + \dots$
$(3_1/2_14_15_1)_{II}$	3281.90	$0.696  3_1\rangle - 0.718  2_14_15_1\rangle + \dots$

<sup>a</sup> from Tamsamani and Herman;<sup>4</sup> <sup>b</sup> in both pairs of Fermi dyads, the vibrational wavefunctions correspond to those for  $J = 3$ ; data for the higher pair of Fermi dyads was kindly provided by Dr A.P. Milce,<sup>43</sup> those for the lower pair are from Vander Auwera *et al.*;<sup>5</sup> the coefficients do depend on  $J$  and in the case of the lower Fermi doublet the relative magnitudes of the contributions change over above  $J = 11$ .<sup>5</sup>

eigenstates can be expressed as almost equal combinations of  $|3_1\rangle$  and  $|2_1(4_15_1)^0\rangle$  as shown in Table 1, whereas mixing with  $\delta$  ( $k = 2$ ) state, *i.e.*  $|2_1(4_15_1)^2\rangle$  is very much weaker and only becomes significant at high rotational levels (see Fig. 6 of ref. 5). Furthermore, the two vibrational bands with their origins at 3281.9 and 3294.84  $\text{cm}^{-1}$  have virtually identical strengths in the IR spectrum of  $\text{C}_2\text{H}_2$ .<sup>34</sup> In the polyad description these levels would both have the quantum numbers  $n_s = 1$ ,  $n_r = 5$ ,  $k = 0$ . Other states in this polyad, such as  $|1_1\rangle$ , have  $g$ -symmetry and are therefore unable to mix with  $|3_1\rangle$  and  $|2_1(4_15_1)^0\rangle$ .

The other states of interest in the present work are the two from the (1,6,1) polyad which are predominantly formed (see Table 1) from the  $|3_1(4_1)^1\rangle$  and  $|2_1(4_25_1)^1\rangle$  zero order states. As Table 1 shows, the situation here is a little more complicated than for the lower Fermi dyad, unequal contributions to this Fermi dyad coming from the two states with  $k = 1$ ,  $|2_1(4_2^25_1^{-1})^1\rangle$  and  $|2_1(4_2^05_1^1)^1\rangle$ . Infrared transitions from the vibrational ground state are allowed to both the  $(3_14_1/2_14_25_1)_{II}$  and  $(3_14_1/2_14_25_1)_I$  levels but are, of course, weaker than the bands associated with the  $(3_1/2_14_15_1)_{I,II}$  dyad where the IR activity is derived from the  $\nu_3$  fundamental.

It is worth noting that these Fermi resonances in  $\text{C}_2\text{H}_2$  are somewhat different from the celebrated Fermi resonance in  $\text{CO}_2$  involving the  $|10^0\rangle$  and  $|02^0\rangle$  zero order states in that molecule. In the latter case, the unperturbed vibrational term values differ by 7.87  $\text{cm}^{-1}$  but the off-diagonal matrix element is large,  $-51.2 \text{ cm}^{-1}$ .<sup>25</sup> However, for the  $(3_1/2_14_15_1)$  dyad in acetylene, once allowance is made for  $\ell$ -type resonances, the zero order splitting is only 0.42  $\text{cm}^{-1}$ , but the off-diagonal matrix element, at 6.47  $\text{cm}^{-1}$ , is appreciably less than in  $\text{CO}_2$ .<sup>25</sup> One effect of the very small zero order splitting in  $\text{C}_2\text{H}_2$  and the slight difference in the rotational constants for the two states (see Table 1) is that the mixing coefficients show significant dependence on the rotational quantum number  $J$ ,<sup>5</sup> and indeed exhibit a crossing at  $J = 11$ , in that below this level the lower vibrational state shows a predominance of  $|2_1(4_15_1)^1\rangle$  but  $|3_1\rangle$  makes the larger contribution above  $J = 11$ .

In the experiments described in the present paper, an infrared-ultraviolet double resonance (IRUVDR) technique is employed to follow: (a) the kinetics of collisionally induced V-V transfer between the components (I and II) of the two Fermi dyads,  $(3_1/2_14_15_1)_{I,II}$  and  $(3_14_1/2_14_25_1)_{I,II}$ , and (b) vibrational relaxation from the coupled states of each dyad. Pulses of IR radiation from a tunable optical parametric oscillator (OPO), the pump laser, are used to excite molecules to one component state of a given Fermi dyad *via* direct IR absorption. As in previous work from this laboratory<sup>14-17</sup> and others,<sup>18-28,30-32</sup> the subsequent fate of the excited molecules has been followed using laser-induced fluorescence (LIF). Tunable UV radiation from a frequency doubled tunable dye laser, the probe laser, excites molecules by absorption in lines within the  $\tilde{A}^1A_u-\tilde{X}^1\Sigma_g^+$  electronic band system. In most of our experiments, the frequency of the dye laser is fixed and the delay between the pulses from the IR pump and UV probe

lasers is varied to provide kinetic information about the evolution of population in particular rovibrational levels in the  $\tilde{X}^1\Sigma_g^+$  ground state. In some experiments, the time delay is fixed and the frequency of the probe laser is scanned in order to record spectra in an effort to identify the vibrational states in  $\tilde{X}^1\Sigma_g^+$  which are populated during the relaxation process.

$\text{C}_2\text{H}_2$  is *trans*-bent ( $C_{2v}$  symmetry, CCH angle = 122.5°) in its  $\tilde{A}^1A_u$  excited electronic state and the CC bond length ( $r_{CC} = 1.375 \text{ \AA}$ ) is appreciably extended compared with its value ( $r_{CC} = 1.208 \text{ \AA}$ ) in the  $\tilde{X}^1\Sigma_g^+$  ground state.<sup>35</sup> Because of the  $g \leftrightarrow u$  optical selection rule, as well as poor Franck-Condon factors, information about the vibrational levels in  $\tilde{A}^1A_u$  has been restricted until recently. In part, this data base has been extended using double resonance techniques,<sup>36</sup> *i.e.*, by populating excited vibrational levels of *ungerade* symmetry in the  $\tilde{X}^1\Sigma_g^+$  state *via* stimulated Raman or infrared (or, in the case, of high overtones, visible) pumping and then observing transitions to vibrational levels of *gerade* symmetry in  $\tilde{A}^1A_u$  to which transitions would be forbidden from the zeroth vibrational level of  $\tilde{X}^1\Sigma_g^+$ . These experiments have revealed that there is also extensive vibrational mixing in the excited  $\tilde{A}^1A_u$  state. The mixed character of the eigenstates in the two Fermi dyads in  $\tilde{X}^1\Sigma_g^+$  whose dynamics are studied here assists our double resonance experiments, since the strength of the UV probe transition is increased by the presence of  $\nu_2$  and  $\nu_4$  excitations in all these vibrational levels. On the other hand, relative populations in different vibrational levels in  $\tilde{X}^1\Sigma_g^+$  cannot be determined because of the difficulty of estimating accurate Frank-Condon factors for bands in the  $\tilde{A}^1A_u-\tilde{X}^1\Sigma_g^+$  system, especially for transitions between heavily mixed states.

The present paper reports the transfer of  $\text{C}_2\text{H}_2$  molecules between the component states of the  $(3_1/2_14_15_1)$  and  $(3_14_1/2_14_25_1)$  dyads in collisions with  $\text{C}_2\text{H}_2$  itself and with  $\text{N}_2$  and  $\text{H}_2$ , as well as vibrational relaxation from each of these dyads induced by collisions with the same collision partners. A preliminary report on the intradyad transfer induced by  $\text{C}_2\text{H}_2-\text{C}_2\text{H}_2$  collisions has been published.<sup>17</sup> The succeeding paper, *i.e.* Part II,<sup>37</sup> reports the measurement of rotational state to rotational state rate coefficients, both for transfer between  $J$  levels within the  $(3_1/2_14_15_1)_{II}$  state in collisions with  $\text{C}_2\text{H}_2$ , Ar, He and  $\text{H}_2$ , and for transfer in  $\text{C}_2\text{H}_2-\text{C}_2\text{H}_2$  collisions from the  $J = 10$  level in  $(3_1/2_14_15_1)_{II}$  to specific  $J$  levels in  $(3_1/2_14_15_1)_I$ . The only earlier measurement of intradyad transfer, from  $(3_1/2_14_15_1)_I$  to  $(3_1/2_14_15_1)_{II}$ , was made by Frost<sup>15</sup> using a related but different method from that employed in the present work. §

There has been more previous work on vibrational relaxation in  $\text{C}_2\text{H}_2$ . Much of this work has emphasised self-relaxation, *i.e.* that in  $\text{C}_2\text{H}_2-\text{C}_2\text{H}_2$  collisions. The results have

§ It should be noted that Frost<sup>15</sup> used the labels I and II in the reverse sense to that employed in the present paper. That is, in his paper I denotes the lower of the two states in the  $(3_1/2_14_15_1)$  dyad, II the upper.

**Table 2** Rate coefficients ( $k_{vr}$ ) and collisional probabilities ( $P$ )<sup>a</sup> for vibrational self-relaxation in C<sub>2</sub>H<sub>2</sub> from previous studies

C <sub>2</sub> H <sub>2</sub>	$k_v/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$P$	Ref.
(3 <sub>1</sub> /2 <sub>1</sub> 4 <sub>1</sub> 5 <sub>1</sub> ) C—H stretch	7.0 × 10 <sup>-11</sup> 7.4 × 10 <sup>-11</sup>	0.14 0.15	16 13
(4 <sub>1</sub> 5 <sub>2</sub> ) <i>trans</i> -bend/ <i>cis</i> -bend	7.0 × 10 <sup>-11</sup>	0.14	16
(2 <sub>1</sub> 4 <sub>1</sub> ) C—C stretch/ <i>trans</i> -bend	2.9 × 10 <sup>-11</sup> 2.9 × 10 <sup>-11</sup>	0.059 0.059	16 23
(4 <sub>2</sub> ) <i>trans</i> -bend (provisional assignment)	3.2 × 10 <sup>-11</sup>	0.065	16
(2 <sub>1</sub> ) C—C stretch	6.5 × 10 <sup>-13</sup>	0.0013	38

<sup>a</sup> Referred to the following rate coefficient for collisions subject to a Lennard-Jones potential: C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>2</sub>: 16.0 Torr<sup>-1</sup> μs<sup>-1</sup> (=4.91 × 10<sup>-10</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>).

been reviewed by Orr<sup>25,29</sup> and are summarised in Table 2. The only extensive information about vibrational relaxation with other collision partners comes from the work of Smith and Warr.<sup>13</sup> They employed the laser-induced vibrational (IR) fluorescence technique to measure the rate coefficients for relaxation from the (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>) dyad in collision with C<sub>2</sub>H<sub>2</sub> and the noble gases. Attempts to investigate the effects of noble gas collisions in the present work were defeated by the rapid quenching of the  $\tilde{A}^1A_u$  state<sup>37</sup> compared with the rates of processes induced by these species in the  $\tilde{X}^1\Sigma_g^+$  state, thereby demonstrating the advantages of the IR vibrational fluorescence method under certain circumstances. There has also been a limited number of previous measurements of the rates of state-to-field vibration-to-vibration (V-V) transfer between coupled vibrational states within the same polyad. These experiments have necessarily been performed on states where such processes are facile. The results are summarised in Table 3.

## Experimental

The apparatus and experimental procedures are similar to those employed in previous IRUVDR experiments on acetylene undertaken in this laboratory.<sup>14-17</sup> Moreover, a short paper describing the present experiments on intradyad V-V transfer in C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>2</sub> collisions has been published.<sup>17</sup> Consequently, only a brief, but self-contained, description of the experimental apparatus and procedures is given here.

Molecules of C<sub>2</sub>H<sub>2</sub> were selectively excited using tunable IR radiation from the OPO, which was pumped by the 1.064 μm output from a seeded Nd:YAG laser (Spectron, model 800). The pulse energy in the idler beam from the OPO at the wavenumbers of transitions within the (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>)<sub>II</sub> ← 0 band (band centre, 3281.9 cm<sup>-1</sup>) and the (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>)<sub>II</sub> ← 0 band (band centre, 3882.4 cm<sup>-1</sup>) was in the range 0.1–0.6 mJ, the fluence at the observation zone was 0.5–5.0 mJ cm<sup>-2</sup>, and the bandwidth was *ca.* 0.3 cm<sup>-1</sup>. The output of the OPO was tuned with the aid of a spectrophone containing 100 Torr of acetylene. In exciting C<sub>2</sub>H<sub>2</sub> to (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>)<sub>II</sub>, the OPO output was tuned to a strong P- or R-branch line in the appropriate

band. However, since rotational selectivity was not required in the present experiments, to access (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>)<sub>II</sub>, the OPO frequency was tuned to that of the Q-branch of the vibrational band. As the rotational constants in the upper and lower levels of the transition differ by only *ca.* 0.005 cm<sup>-1</sup>, several rotational transitions lie within the bandwidth of the pump laser and this method partially compensates for the intrinsic weakness of this band relative to that carrying the oscillator strength of the  $\nu_3$  fundamental. The spectrum published as Fig. 1 of ref. 17 shows that about 7–8 rotational levels in (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>)<sub>II</sub> are directly populated using this method.

As before, the UV probe radiation was provided by a tunable dye laser (Lambda Physik, FL2002) pumped by an excimer laser operating on XeCl, though a different excimer laser (Lambda-Physik LPX110) was used than in earlier experiments from this laboratory.<sup>14-16</sup> The fundamental output from the dye laser was frequency-doubled in β-barium borate (BBO) to provide UV radiation between 240 and 250 nm.

The pump and probe laser beams counter-propagated through a simple cylindrical cell which was fitted with CaF<sub>2</sub> windows at each end, and the fluorescence induced by the dye laser was observed perpendicular to the laser beams through a quartz window. A photomultiplier tube (EMI model 9781R), an optical filter and a collecting lens were mounted in a housing which was clamped to the centre of the cell. The equipment for controlling the firing of the lasers and for recording, accumulating and analysing LIF signals was the same as that described previously.<sup>14-16</sup>

In the present experiments in which LIF signals were recorded as a function of the time delay between the pulses from the pump and probe lasers, the IR pulse from the OPO prepared C<sub>2</sub>H<sub>2</sub> in one component state of a Fermi dyad and the UV pulse from the dye laser was tuned to a transition from the other Fermi component of the same pair. In experiments on each dyad, lines in UV bands leading to the mixed (3<sub>1</sub>4<sub>1</sub>/3<sub>1</sub>6<sub>1</sub>) vibrational levels in the  $\tilde{A}^1A_u$  state were chosen for LIF probing. These experiments yielded the kinetic behaviour of the population in the initially unexcited component state of the dyad. The delays were synchronised using a pulse generator (Stanford Research Systems, model DG535) and controlled *via* an IBM-compatible PC *via* an IEEE interface. Typically, the signals at each time delay were averaged over 70–100 laser shots and they were normalised to the pulse energy from the IR pump laser, which had a much greater shot-to-shot variability than the UV probe laser.

The C<sub>2</sub>H<sub>2</sub> used in these experiments was provided by BOC (Industrial Grade). It was purified by several freeze-pump-thaw cycles. N<sub>2</sub> and H<sub>2</sub> were taken from cylinders and stored in Pyrex bulbs, following transfer from a bulb fitted with a cold finger immersed in liquid N<sub>2</sub>. All measurements were made at room temperature (295 ± 5 K).

## Analysis

The aim in the present experiments was to determine rate coefficients for two kinds of collisional process: (a) those which transfer excited C<sub>2</sub>H<sub>2</sub> molecules from one component state of a Fermi dyad to the other component state, and (b)

**Table 3** State-to-field rate coefficients for intradyad V-V transfer from selected rotational levels in C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>2</sub> collisions

C <sub>2</sub> H <sub>2</sub>	( $E_v/hc$ )/cm <sup>-1</sup>	$k_v/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Ref.
(3 <sub>1</sub> /2 <sub>1</sub> 4 <sub>1</sub> 5 <sub>1</sub> ) <sub>I</sub> , $J = 12 \rightarrow$ (3 <sub>1</sub> /2 <sub>1</sub> 4 <sub>1</sub> 5 <sub>1</sub> ) <sub>I</sub> , all $J$	3295	1.5 × 10 <sup>-10</sup>	15
(1 <sub>1</sub> 2 <sub>1</sub> 3 <sub>1</sub> 4 <sub>2</sub> ), $J = 4 \rightarrow$ (3 <sub>3</sub> ), all $J$	9640	4.0 × 10 <sup>-11</sup>	21
(2 <sub>4</sub> 4 <sub>3</sub> 5 <sub>3</sub> ), $J = 12 \rightarrow$ (2 <sub>1</sub> 3 <sub>3</sub> ) <sub>I</sub> , all $J$	11 600	9.7 × 10 <sup>-11</sup>	27
(2 <sub>4</sub> 4 <sub>3</sub> 5 <sub>3</sub> ), $J = 12 \rightarrow$ (2 <sub>1</sub> 3 <sub>3</sub> ) <sub>II</sub> , all $J$	11 600	7.4 × 10 <sup>-11</sup>	27

those which relax  $C_2H_2$  molecules from this coupled pair of levels to lower vibrational states.<sup>¶</sup> Quantitative data have been obtained for three collision partners,  $C_2H_2$ ,  $N_2$  and  $H_2$ . A complication in analysing the experimental results is that three processes of relaxation occur following excitation by the pump laser: rotational relaxation, equilibration of population within the Fermi dyad, and relaxation from the coupled vibrational levels. Furthermore, the time-scales of the three processes are not very different, although the relative rates depend both on the Fermi dyad which is excited and observed and on the composition of the gas mixture, since the relative values of the rate coefficients for the three processes do vary between  $C_2H_2$ ,  $N_2$  and  $H_2$ .

Rate coefficients for rotational relaxation, *i.e.* for the total removal of  $C_2H_2$  from selected rotational states in collisions with other  $C_2H_2$  molecules, have been determined by Frost and Smith<sup>14</sup> for rotational levels in both  $(3_1/2_14_15_1)_{II}$  and  $(3_1/2_14_15_1)_I$  and by others<sup>19,27,30,31</sup> for particular  $J$  states in other vibrational levels. The rate coefficients which Frost and Smith determined for total transfer out of the  $J = 12$  rotational level of the lower component of the  $(3_1/2_14_15_1)$  dyad with  $C_2H_2$ ,  $N_2$  and  $H_2$  were  $9.5 \times 10^{-10}$ ,  $7.4 \times 10^{-10}$  and  $3.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The rate coefficients for rotational relaxation in  $C_2H_2$ - $C_2H_2$  collisions have been found to be essentially independent of initial rotational and vibrational state, and we expect the values of the rate coefficients determined by Frost and Smith to hold for all the vibrational levels considered in the present work. The values are at least an order of magnitude larger than the rate coefficients for vibrational relaxation out of the coupled levels of the two Fermi dyads,  $(3_1/2_14_15_1)_{II}$  and  $(3_1/2_14_15_1)_I$ , which have been measured in the present or previous<sup>13, 16</sup> work.

However, the rate coefficient for V-V transfer between the states of  $(3_1/2_14_15_1)_{II}$  induced by  $C_2H_2$ - $C_2H_2$  collisions, which is derived here and which was measured by Frost,<sup>15</sup> has a value intermediate between those for rotational and vibrational relaxation and is 'uncomfortably' close to that for rotational relaxation. In the analysis which is described below and which is used to derive rate coefficients for intradyad vibrational state transfer, it is assumed that either rotational relaxation is appreciably faster than intradyad V-V transfer or that its rate does not depend significantly on the degree of rotational relaxation. To justify this assumption, (a) we were careful in our choice of experimental parameters, and (b) we examined the results carefully for evidence of effects attributable to rotational non-equilibrium. In the case of excitation to the  $(3_1/2_14_15_1)$  dyad, rotational equilibration was facilitated by the fact that excitation *via* Q-branch transitions directly populates a number of rotational levels (see above), rather than a single rotational level. In order to minimise any effects in the case of measurements on the  $(3_1/2_14_15_1)_{II}$  levels, molecules were excited to a rotational level ( $J = 10$ ) in the  $(3_1/2_14_15_1)_{II}$  state near to the maximum of the rotational distribution and observations of population in  $(3_1/2_14_15_1)_I$  were made on a rotational level close to the highest populated. In order to demonstrate that rotational equilibration is extensive on a time scale which is short relative to that used in our kinetic measurements, in Fig. 1 we display an LIF spectrum of the  $\tilde{A}(3_1/2_14_15_1)_{II}$ - $\tilde{X}(3_1/2_14_15_1)_{II}$  band taken at a short delay time. Finally, we point out that the experiments of Frost<sup>15</sup> and ourselves<sup>34</sup> demonstrate (a) that, when collisions transfer

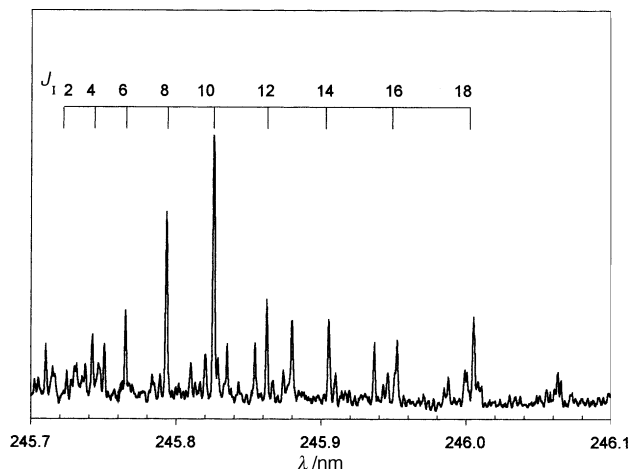
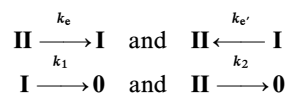


Fig. 1 LIF spectrum from the  $(3_1/2_14_15_1)_{II}$  state recorded at a pressure of 249 mTorr  $C_2H_2$  and with a 300 ns delay between the IR pump and UV probe lasers. The output of the pump laser was tuned to excite  $J = 10$  in the  $(3_1/2_14_15_1)_{II}$  state. The time delay corresponds to about twice the rotational relaxation time at this pressure of  $C_2H_2$ .

molecules between dyad states, they do so to quite a wide range of rotational levels, and (b) that the rate coefficient which is derived here from a range of initial rotational levels and with the assumption of either rotational equilibration or a lack of dependence of rates on initial  $J$  is similar to that obtained for transfer from a defined initial rotational level,  $J = 12$  by Frost<sup>15</sup> and  $J = 10$  by ourselves.<sup>37</sup>

If one assumes that rotational relaxation does not significantly influence the observations of how the LIF signals vary with time, the processes which need to be considered in analysing the kinetics of the system can be expressed in the equations:



Here  $k_i$  represent pseudo-first-order rate coefficients (a)  $k_e$  and  $k_{e'}$ , for transfer between a pair of states (II and I) which can be coupled *via* collisional processes, and (b)  $k_2$  and  $k_1$ , for relaxation out of these states to lower energy levels denoted by 0. The general relationships between the populations in two collisionally coupled states and the rate constants for transfer between them and removal from them has been derived and cited many times, notably in relation to vibrational relaxation in systems where near-resonant vibration-to-vibration energy exchange is possible between two components of the gas mixture.<sup>39</sup> If state II is initially excited at zero time to produce a concentration  $[\text{II}]_0$ , solution of the kinetic equations yields expressions of the form:

$$[\text{II}] = [\text{II}]_0 \{A'_1 \exp(-\lambda_1 t) + A''_1 \exp(-\lambda_2 t)\} \quad (2)$$

$$[\text{I}] = [\text{II}]_0 A_{II} \{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \quad (3)$$

In general, it is not straightforward to relate  $\lambda_1$  and  $\lambda_2$  to the four first-order rate constants,  $k_e$ ,  $k_{e'}$ ,  $k_1$  and  $k_2$ . However, there are a variety of simplifying cases. In the present situation, two assumptions can reasonably be made. The first is that  $k_e$  and  $k_{e'}$  are identical, since the difference in energy between the component states of each Fermi dyad is very small (see Table 1) relative to  $k_B T$ , and that both are given by the equation

$$k_e = k_{e'} = k_{id}^{C_2H_2}[C_2H_2] + k_{id}^M[M] \quad (4)$$

where  $k_{id}^X$  is the second-order rate constant for transfer between components of that Fermi dyad in collisions with gas

¶ Here we note that collisional transfer from one component state of a Fermi dyad to the other is likely to be a near-resonant intramolecular V-V process in which the excited molecule undergoes a transition between levels of very nearly equal energy and the collision partner remains in its original vibrational state. On the other hand, the loss of population from the Fermi dyad probably occurs by intermolecular V-V exchange for which several near-resonant pathways exist.

X, which can be C<sub>2</sub>H<sub>2</sub> itself or an added gas M. The second assumption is that  $k_1$  and  $k_2$  are identical, since the wavefunctions for states I and II of each Fermi dyad are so similar (further justification for this assumption is given below), and that both are given by

$$k_1 = k_2 = k_{\text{vr}}^{\text{C}_2\text{H}_2}[\text{C}_2\text{H}_2] + k_{\text{vr}}^{\text{M}}[\text{M}] + k_{\text{diff}}/p \quad (5)$$

where  $k_{\text{vr}}^{\text{X}}$  is the second-order rate coefficient for vibrational relaxation from the I, II states in collisions with X = C<sub>2</sub>H<sub>2</sub> or M and  $k_{\text{diff}}/p$  allows for diffusion of excited molecules out of the observation zone in a gas sample of particular composition at total pressure  $p$ . With these assumptions

$$\lambda_2 = k_1 + 2k_e = (k_{\text{vr}}^{\text{C}_2\text{H}_2} + 2k_{\text{id}}^{\text{C}_2\text{H}_2})[\text{C}_2\text{H}_2] + (k_{\text{vr}}^{\text{M}} + 2k_{\text{id}}^{\text{M}})[\text{M}] + k_{\text{diff}}/p \quad (6a)$$

$$\lambda_1 = k_1 = k_{\text{vr}}^{\text{C}_2\text{H}_2}[\text{C}_2\text{H}_2] + k_{\text{vr}}^{\text{M}}[\text{M}] + k_{\text{diff}}/p \quad (6b)$$

The form of these relationships means that the first-order rate coefficients  $\lambda_2$  and  $\lambda_1$  that are obtained by analysing the traces of LIF signal *vs.* time from either state II or state I can be unequivocally assigned as  $k_1 + 2k_e$  and  $k_1$ . Observation of how these rate constants vary with total pressure and mixture composition then allows the rate constants  $k_{\text{id}}^{\text{C}_2\text{H}_2}$ ,  $k_{\text{id}}^{\text{M}}$ ,  $k_{\text{vr}}^{\text{C}_2\text{H}_2}$  and  $k_{\text{vr}}^{\text{M}}$  to be determined.

## Results and discussion

We have performed two kinds of experiments in the present work. In the majority of experiments, LIF signals were recorded at different delay times following IR excitation of C<sub>2</sub>H<sub>2</sub> molecules to one or more rotational levels in one component of one or other of the Fermi dyads (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>) or (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>). The frequency of the UV probe laser was tuned to a strong line from either the component which was directly excited or to a transition from the other component of the same dyad. Traces of LIF signal *vs.* delay were recorded and interpreted according to the analysis described in the previous section of this paper. In addition to these kinetic experiments, a smaller number of spectroscopic experiments were carried out in which the frequency of the UV probe laser was scanned to record spectra at a fixed time delay after C<sub>2</sub>H<sub>2</sub> molecules were excited by the IR pump laser. The results of these two sets of experiments are described and discussed separately below in sub-sections (a) and (c).

### (a) Vibrational relaxation of C<sub>2</sub>H<sub>2</sub> within and from the Fermi dyad levels (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>) and (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>): Results

Fig. 2 shows typical records of how the LIF signals from component states of the two Fermi dyads varied with the delay between the pulses from the pump and probe lasers in samples of pure C<sub>2</sub>H<sub>2</sub>. Rate coefficients for transfer between the components of the (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>) dyad were determined from measurements like that shown in Fig. 2(a). That is, the pump laser excited molecules to the one component state, in this case (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>)<sub>I</sub>, and the probe laser monitored the evolution of population in the other component state, here (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>)<sub>II</sub>, by recording LIF signals. The variation of these LIF signals with time was then fitted to a function of the form given in eqn. (3) to extract values of the first-order coefficients  $\lambda_1$  and  $\lambda_2$ . This procedure was repeated for samples of C<sub>2</sub>H<sub>2</sub> over the pressure range 50–300 mTorr. At these low pressures, some allowance has to be made for any decrease in the LIF signals due to excited molecules diffusing out of the observation zone. Consequently, to extract values of the rate coefficients for intradyad (II ↔ I) transfer and vibrational relaxation (I, II → 0), the values of  $\lambda_1$  and  $\lambda_2$  derived from the fits were multiplied by [C<sub>2</sub>H<sub>2</sub>] and plotted against [C<sub>2</sub>H<sub>2</sub>]<sup>2</sup> as suggested by eqn. (6a) and (6b). The resultant plots are shown in Fig. 3. The slopes of the lines correspond to  $k_{\text{vr}}^{\text{C}_2\text{H}_2}$  and  $(k_{\text{vr}}^{\text{C}_2\text{H}_2} + 2k_{\text{id}}^{\text{C}_2\text{H}_2})$

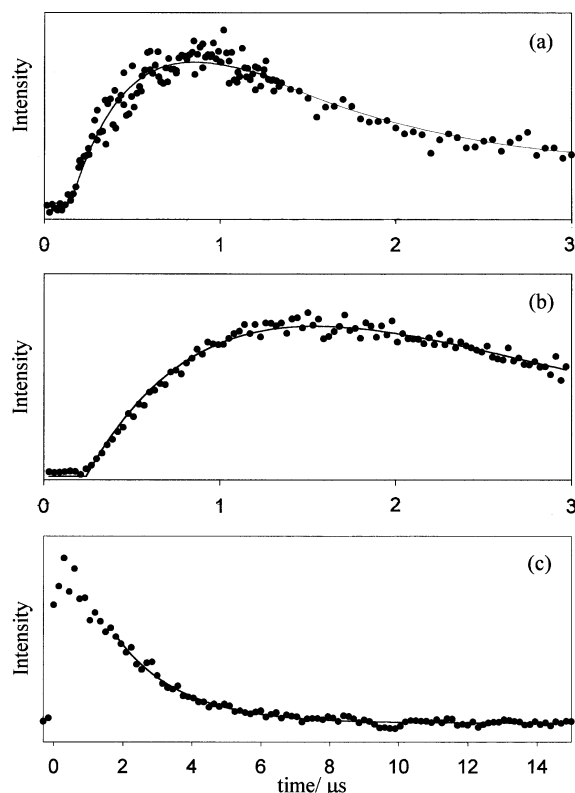


Fig. 2 Traces of LIF signal *vs.* time from samples of pure acetylene: (a) 198 mTorr C<sub>2</sub>H<sub>2</sub>, exciting (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>)<sub>I</sub>, observing (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>)<sub>II</sub>; (b) 224 mTorr C<sub>2</sub>H<sub>2</sub>, exciting (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>)<sub>I</sub>, observing (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>)<sub>II</sub>; (c) 213 mTorr C<sub>2</sub>H<sub>2</sub>, exciting (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>)<sub>I</sub>, observing (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>)<sub>II</sub>.

and the intercepts to  $k_{\text{diff}}$ . The rate coefficients  $k_{\text{vr}}^{\text{C}_2\text{H}_2}$  and  $2k_{\text{id}}^{\text{C}_2\text{H}_2}$  which are derived from the slopes of these graphs are listed in Table 4. The value of  $k_{\text{id}}^{\text{C}_2\text{H}_2}$  is in good agreement with that given previously,<sup>17</sup> which was derived from the same set of results but by a somewhat different analysis.

As indicated in Fig. 2, measurements of two kinds were carried out on the (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>) Fermi dyad. First, the decay was followed from the directly populated state, in this case (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>)<sub>II</sub>, as shown in Fig. 2(c). Data were recorded over the range 50–400 mTorr of C<sub>2</sub>H<sub>2</sub>. In these experiments, to avoid the need to allow for diffusion effects, the total pressure was kept constant by dilution with argon to a total pressure of 2 Torr. Argon has been shown (see below) to cause both intradyad transfer and vibrational relaxation at rates more than 100 times slower than C<sub>2</sub>H<sub>2</sub> but it does inhibit diffusion

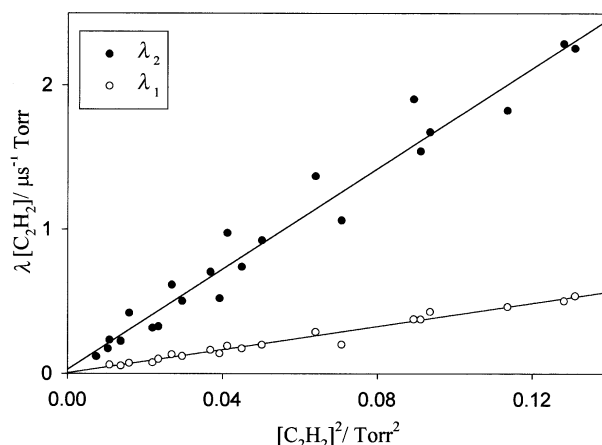


Fig. 3 Plots of (a)  $\lambda_1[\text{C}_2\text{H}_2]$  and (b)  $\lambda_2[\text{C}_2\text{H}_2]$  against the square of the acetylene concentration from traces obtained by exciting (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>)<sub>I</sub> and observing LIF signals from (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>)<sub>II</sub>.

**Table 4** Rate coefficients and collisional probabilities ( $P$ )<sup>a</sup> for intradyad transfer between ( $k_{id}$ ) and vibrational relaxation from ( $k_{vr}$ ) the ( $3_{1/2,1,4_1,5_1}$ ) and ( $3_{1,4_1/2,1,4_2,5_1}$ ) Fermi dyads in  $C_2H_2$

	$k_{id}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		$k_{vr}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
$C_2H_2$	$(3_{1/2,1,4_1,5_1})$ $(2.1 \pm 0.2)^b \times 10^{-10}$ 0.43	$(3_{1,4_1/2,1,4_2,5_1})$ $(3.2 \pm 0.6) \times 10^{-11}$ 0.065	$(3_{1/2,1,4_1,5_1})$ $(1.0 \pm 0.1) \times 10^{-10}$ 0.20	$(3_{1,4_1/2,1,4_2,5_1})$ $(6.9 \pm 0.6) \times 10^{-11}$ 0.14
$H_2$	$(8.6 \pm 1.0) \times 10^{-11}$ 0.12	$(1.4 \pm 0.1) \times 10^{-12}$ 0.0019	$(1.2 \pm 0.2) \times 10^{-11}$	$(1.6 \pm 0.1) \times 10^{-11}$ 0.022
$N_2$	$(2.6 \pm 0.8) \times 10^{-11}$ 0.070	$(9 \pm 4) \times 10^{-13}$ 0.002	$(1.9 \pm 0.6) \times 10^{-12}$ 0.005	$(7.3 \pm 1.6) \times 10^{-13}$ 0.0020

<sup>a</sup> Referred to the following rate coefficients for collisions subject to a Lennard-Jones potential:  $C_2H_2-C_2H_2$ :  $16.0 \text{ Torr}^{-1} \mu\text{s}^{-1}$  ( $=4.91 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ );  $C_2H_2-H_2$ :  $23.5 \text{ Torr}^{-1} \mu\text{s}^{-1}$  ( $=7.21 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ );  $C_2H_2-N_2$ :  $12.2 \text{ Torr}^{-1} \mu\text{s}^{-1}$  ( $=3.74 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). <sup>b</sup> Errors are cited at the  $2\sigma$  level including only random errors.

and increase the rate of rotational relaxation. Strictly, the traces of LIF signals from  $(3_{1,4_1/2,1,4_2,5_1})_{II}$  vs. time will follow the form given in eqn. (2). However, because intradyad transfer is significantly faster than vibrational relaxation, i.e.  $k_e > k_1$  in eqn. (6),  $\lambda_1 \gg \lambda_2$  and the signals at relatively long times will fit a single exponential function with  $\lambda_1 = k_1$ , as shown in Fig. 2(c) and tested by starting the fit at different delay times. The data obtained from such experiments constitute most of the points shown in Fig. 4(a).

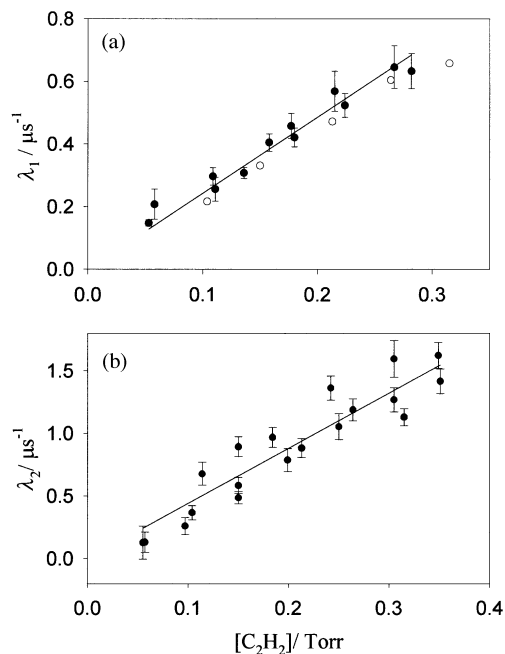
A second series of experiments on the upper Fermi dyad was performed in which the evolution of population in the initially unexcited component state, i.e.  $(3_{1,4_1/2,1,4_2,5_1})_I$ , was followed,  $C_2H_2$  molecules having been excited to the lower component state using IR pumping in the Q-branch of the  $(3_{1,4_1/2,1,4_2,5_1})_I \leftarrow 0$  band. These traces were recorded over a shorter time delay, as shown in Fig. 2(b). This form is then fitted in accord with eqn. (3), providing a second determination of  $\lambda_1 = k_1$ . These results are also plotted in Fig. 4(a). The agreement of these data with those obtained from analysing the signals from  $(3_{1,4_1/2,1,4_2,5_1})_{II}$  is excellent and the gradient of the line in Fig. 4(a) corresponds to the rate coefficient for vibrational self-relaxation of  $C_2H_2$  from the coupled dyad states  $(3_{1,4_1/2,1,4_2,5_1})_{I, II}$  which is listed in Table 4.

Having obtained a 'best' value for  $k_{vr}^{C_2H_2}$  the complete traces of the signals from  $(3_{1,4_1/2,1,4_2,5_1})_I$  were fitted, constraining  $\lambda_1$  to be consistent with that value. The result of one such fit to

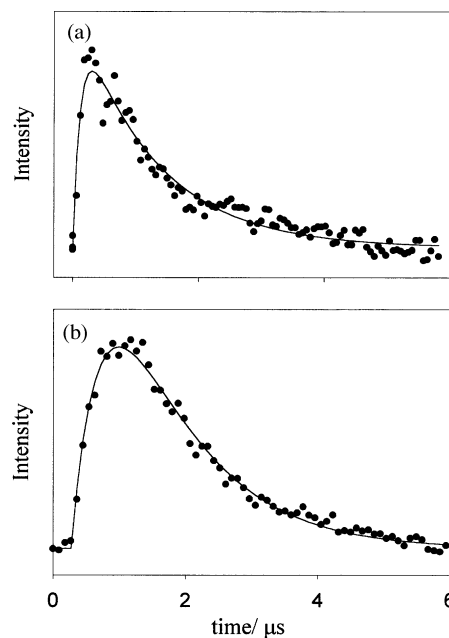
the early part of such a trace is shown in Fig. 2(b). The plot of  $\lambda_2$  values against  $[C_2H_2]$  from which the rate coefficient for intradyad transfer could be deduced is shown in Fig. 4(b) and the value of  $k_{id}^{C_2H_2}$  is listed in Table 4.

We had hoped to investigate intradyad transfer and vibrational relaxation in collisions of  $C_2H_2$  with at least some of the noble gases, since the simplicity of such collision partners would give the best chance for comparison with *ab initio* theoretical calculations. In practice, it proved impossible to determine rate coefficients for these processes on account of their relative slowness and the rapid rates at which even helium and argon quench the  $\tilde{A}^1A_u$  state of  $C_2H_2$ .<sup>40</sup> Our measurements do indicate that the rate coefficients  $k_{vr}^{He}$  and  $k_{vr}^{Ar}$  have upper limits of ca.  $4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in the case of the  $(3_{1/2,1,4_1,5_1})$  dyad.

Experiments were successful in obtaining rate coefficients for intradyad transfer and vibrational relaxation induced by collisions with  $H_2$  and  $N_2$ . In these experiments, a pressure of acetylene, typically 150 mTorr, was first admitted to the cell and then progressively greater pressures of the other gas was added. In all these experiments,  $C_2H_2$  molecules were excited to one component state of the dyad and LIF signals were observed from the other state. Typical traces obtained in the presence of  $H_2$  are shown in Fig. 5. Such traces were analysed as before by fitting the signals to the form given by eqn. (3). In the case of  $C_2H_2-H_2$  mixtures, corrections for the effects of diffusion were made by performing preliminary experiments to



**Fig. 4** (a) Plots of  $\lambda_1$  vs.  $[C_2H_2]$  obtained both by analysing LIF traces from  $(3_{1,4_1/2,1,4_2,5_1})_{II}$  (●) and from  $(3_{1,4_1/2,1,4_2,5_1})_I$  (○) having excited  $(3_{1,4_1/2,1,4_2,5_1})_{II}$ ; (b) Plots of  $\lambda_2$  vs.  $[C_2H_2]$  by analysing LIF traces from  $(3_{1,4_1/2,1,4_2,5_1})_I$ , having excited  $(3_{1,4_1/2,1,4_2,5_1})_{II}$ . In all cases, the total pressure was kept constant at 2 Torr by adding argon.



**Fig. 5** Traces of LIF signal vs. time for mixtures of  $C_2H_2$  in  $H_2$ : (a) from  $(3_{1/2,1,4_1,5_1})_I$  following excitation to  $(3_{1/2,1,4_1,5_1})_{II}$  in a mixture containing 163 mTorr  $C_2H_2$  and 1.07 Torr  $H_2$ ; (b) from  $(3_{1,4_1/2,1,4_2,5_1})_I$  following excitation to  $(3_{1,4_1/2,1,4_2,5_1})_{II}$  in a mixture containing 176 mTorr  $C_2H_2$  and 1.27 Torr  $H_2$ .

determine  $k_{\text{diff}}$  in eqn. (5). For  $\text{C}_2\text{H}_2\text{-N}_2$  mixtures,  $k_{\text{diff}}$  was estimated from the experimentally determined value for pure  $\text{C}_2\text{H}_2$  and the relationship between the diffusion coefficient  $D$  and  $k_{\text{diff}}$  used here, *via* the solutions for the mass transport equations obtained by Bialkowski *et al.*<sup>41</sup>

Plots of both  $\lambda_1$  and  $\lambda_2$ , with diffusion effects subtracted, *vs.*  $[\text{H}_2]$  and  $[\text{N}_2]$  are shown in Fig. 6. The gradients of these plots and similar ones for  $(3_1/2_1/4_1/5_1)$  yield the rate coefficients which are listed in Table 4 for intradyad transfer ( $k_{\text{id}}^{\text{H}_2}$  and  $k_{\text{id}}^{\text{N}_2}$ ) and for vibrational relaxation ( $k_{\text{vr}}^{\text{H}_2}$  and  $k_{\text{vr}}^{\text{N}_2}$ ) for both the  $(3_1/2_1/4_1/5_1)$  and  $(3_1/4_1/2_1/4_2/5_1)$  dyads.

### (b) Vibrational relaxation of $\text{C}_2\text{H}_2$ within and from the Fermi dyad levels $(3_1/2_1/4_1/5_1)$ and $(3_1/4_1/2_1/4_2/5_1)$ : Discussion

Collision-induced energy transfer in small polyatomic molecules in the presence of perturbations, particularly transfer between components of a Fermi dyad, has been reviewed several times in the recent past.<sup>25,29,42</sup> In cases like the present ones, where the two components of the Fermi dyads are separated by much less than  $k_{\text{B}}T$ , so that little energy has to be transferred into the relative translational motion of the collision partners, the probability of transfer between the two components will depend primarily on the magnitude of matrix elements involving the vibrational wavefunctions of the two eigenstates. Despite the fact that each of the eigenstates comprises a strong mixture of the same zero order states, Orr and Smith<sup>42</sup> stressed that one should beware of assuming that transfer between the eigenstates should necessarily be facile, since a consideration of the vibrational matrix element suggests that destructive interference can occur between individually sizeable terms, with the result that the overall value of the matrix element may be quite small.

Thus, if the two states  $|\Psi_{\text{I}}\rangle$  and  $|\Psi_{\text{II}}\rangle$  of a Fermi dyad can be described in terms of the wavefunctions  $|v_{\text{a}}\rangle$  and  $|v_{\text{b}}\rangle$  for two zero order states, *i.e.*<sup>29</sup>

$$|\Psi_{\text{I}}\rangle = \cos \theta |v_{\text{a}}\rangle + \sin \theta |v_{\text{b}}\rangle \quad (7a)$$

$$|\Psi_{\text{II}}\rangle = -\sin \theta |v_{\text{a}}\rangle + \cos \theta |v_{\text{b}}\rangle \quad (7b)$$

where  $\cos \theta$  and  $\pm \sin \theta$  are perturbation-induced mixing coefficients, then the matrix element for a transition induced by

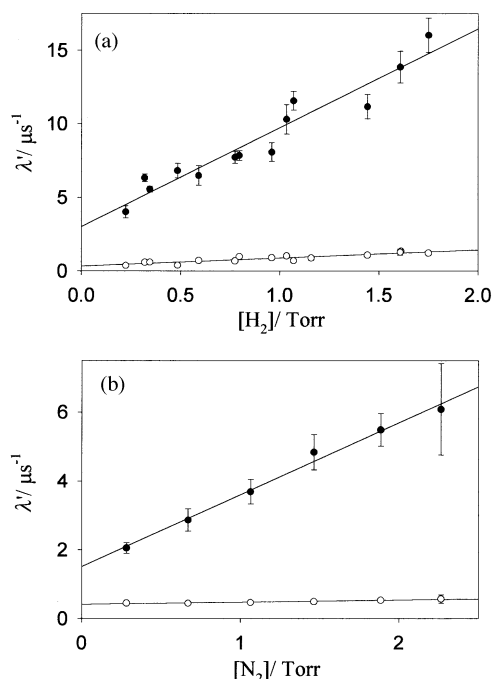


Fig. 6 Plots of  $\lambda' = \lambda_1 - k_{\text{diff}}/p$  (open symbols) and  $\lambda' = \lambda_2 - k_{\text{diff}}/p$  (closed symbols), derived from measurements on the  $(3_1/2_1/4_1/5_1)$  Fermi dyad *vs.* (a)  $[\text{H}_2]$  and (b)  $[\text{N}_2]$ .

the operator  $V$  is<sup>29</sup>

$$\langle \Psi_{\text{I}} | V | \Psi_{\text{II}} \rangle = \frac{1}{2} \sin 2\theta \{ \langle v_{\text{b}} | V | v_{\text{b}} \rangle - \langle v_{\text{a}} | V | v_{\text{a}} \rangle \} + \cos 2\theta \langle v_{\text{a}} | V | v_{\text{b}} \rangle \quad (8)$$

Where the mixing is strong (*i.e.*  $\theta = \pi/4$ ), the dominant terms on the right-hand side are the first two. As they have different signs, the magnitude of the matrix element depends on their relative values. In some cases, they may cancel almost entirely so that transfer between the component states of a dyad is comparatively inefficient.<sup>42</sup>

In seeking to explain the rate constants for V-V intradyad transfer that have been measured in the present work it is necessary to consider at least three features of the results. Firstly, the collisional probabilities are quite high, especially for relaxation within the  $(3_1/2_1/4_1/5_1)$  dyad in  $\text{C}_2\text{H}_2\text{-C}_2\text{H}_2$  collisions. Secondly, the collisional probabilities depend quite strongly on collision partner, those with  $\text{N}_2$  and  $\text{H}_2$  being roughly an order-of-magnitude less than that for  $\text{C}_2\text{H}_2$ , with transfer by collisions with He and Ar being too small to measure. Finally, for all three collision partners, the rates of relaxation within the  $(3_1/2_1/4_1/5_1)$  dyad are 5–10 times faster than those within the  $(3_1/4_1/2_1/4_2/5_1)$  dyad.

As shown in Table 1, the lower dyad on which measurements have been made, *i.e.*  $(3_1/2_1/4_1/5_1)_{\text{I,II}}$ , is a close approximation to the simplest case in which only two zero order states,  $|3_1\rangle$  and  $|2_1/4_1/5_1\rangle$ , contribute significantly to the wavefunctions of the two eigenstates. For illustrative purposes, Orr<sup>25,29</sup> has considered the evaluation of the matrix element represented in eqn. (8) for the case of this dyad using a ‘breathing sphere’ potential<sup>1</sup> of the type

$$V = V_0 \exp(-R/L) \exp(2 \sum \alpha_j Q_j) \quad (9)$$

where  $R$  is the separation of the centres of mass of the collision partners,  $L$  is the effective range of the intermolecular repulsion and  $Q_j$  are mass-weighted normal co-ordinates. The  $\alpha_j$  represent the displacements of ‘surface atoms’ and are related to the normal mode co-ordinates  $Q_j$ . According to this model, the square of the vibrational matrix element, *i.e.*  $|\langle \Psi_{\text{I}} | V | \Psi_{\text{II}} \rangle|^2$  is less than  $10^{-4}$ , and therefore much less than the experimentally determined value.

In the light of this result, Orr<sup>29</sup> suggested that the high probability for transfer between the two components of the  $(3_1/2_1/4_1/5_1)_{\text{I,II}}$  dyad might be due to the role of anharmonic terms in the potential which could make the two diagonal terms on the right-hand side of eqn. (8) very different. In addition, Orr proposed<sup>29</sup> that the facile transfer between  $(3_1/2_1/4_1/5_1)_{\text{I}}$  and  $(3_1/2_1/4_1/5_1)_{\text{II}}$  might be connected with the fact that the splitting between the zero order states is so small (only  $0.42 \text{ cm}^{-1}$  at  $J = 0$  when allowance is made for the  $\ell$ -resonance perturbations) and the mixing coefficients depend on  $J$ . Indeed, below  $J = 11$ , the rotational levels of the lower component [*i.e.* state II] have a higher contribution from the zero order state  $|3_1\rangle$  whereas this situation reverses above  $J = 11$ .

It is also possible that it is long-range attractive terms in the intermolecular potential which makes the two diagonal terms in the right-hand side of eqn. (8) sizeable and different. Given the magnitude of the collisional probabilities, this is an attractive proposition since such changes could occur at long-range and therefore in collisions with large impact parameters. Furthermore, it seems more likely to explain the strong dependence on collision partner, since little dependence of the intradyad V-V transfer probabilities would be expected for such near-resonant processes if repulsive interactions were totally responsible. The suggested importance of long-range forces in inducing intradyad V-V transfer bears a superficial resemblance to the theory of Sharma and Brau<sup>1,44</sup> for intermolecular V-V exchange. However, one should take note of differences in the vibrational matrix elements in the two cases.

For intradyad V–V transfer, the important terms in the matrix elements are diagonal in the wavefunctions for the zero order vibrational states whereas in Sharma–Brau theory they are not, being like that given as the last term on the right-hand side of eqn. (8).

Orr's proposals were made in the light of earlier experiments from this laboratory by Frost.<sup>15</sup> In those experiments, a somewhat different method was employed to find  $k_{id}$  from that employed in the present set of experiments. Molecules of  $C_2H_2$  were excited to  $J = 12$  in the upper component state of the  $(3_1/2_14_15_1)$  dyad and the rate of intradyad transfer determined by observing the intensities of rotational lines from the lower  $(3_1/2_14_15_1)_I$  state at short delays between the pulses from the IR pump and UV probe lasers. In this way, Frost<sup>15</sup> determined  $k_{id} = (1.5 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for intradyad V–V transfer in  $C_2H_2$ – $C_2H_2$  collisions. As the time delays were only a fraction of the rotational relaxation time, this rate coefficient relates to intradyad transfer from the specific rotational level  $J = 12$  in  $(3_1/2_14_15_1)_I$ , rather than from a thermal, or near-thermal, distribution over rotational levels in  $(3_1/2_14_15_1)_I$ , as in the present work. The fact that the rate coefficient which we measure is not greatly different from the state-to-field value measured by Frost<sup>15</sup> appears to imply that the rate coefficients for transfer from specific  $J$  levels in  $(3_1/2_14_15_1)_I$  to  $(3_1/2_14_15_1)_I$  do not depend strongly on initial  $J$ . Results from new experiments of the kind performed by Frost are reported and discussed in Part II.<sup>34</sup>

Braun's analysis on the results of Frost's experiments,<sup>15</sup> Orr<sup>25</sup> determined the ratio ( $R$ ) of the  $J$ -independent reduced matrix elements as

$$R = \langle 2_14_15_1 | V | 2_14_15_1 \rangle / \langle 3_1 | V | 3_1 \rangle = 0.45 \pm 0.05 \quad (10)$$

although an equally valid solution is the inverse of this result; *i.e.*  $R = 2.2$ . This analysis emphasises that rapid intradyad transfer must arise as a result of the large difference in the two diagonal terms in the vibrational matrix element. These points, and the influence of the  $J$ -dependence of the mixing coefficients on the state-to-state rate coefficients for transfer from state I to state II are considered further in Part II.<sup>34</sup>

We also report in Table 4 the rate coefficient for intradyad V–V transfer between the two components of the  $(3_14_1/2_14_25_1)$  dyad. Although this process is also rapid, it is a factor of seven slower than the equivalent process in the  $(3_1/2_14_15_1)$  dyad. The most likely explanation for this difference would appear to be that both the diagonal terms in the matrix element are reduced to similar degrees from their values for the  $(3_1/2_14_15_1)$  by the introduction of an extra quantum of excitation in the  $\nu_4$  vibration. Alternatively, and more strictly, one should note that the vibrational matrix element no longer assumes the simple form given in eqn. (8), because there are now three zero order states,  $|3_1(4_1)^1\rangle$ ,  $|2_1(4_2^25_1^{-1})^1\rangle$  and  $|2_1(4_2^05_1^1)^1\rangle$ , which make appreciable contributions to the eigenstates of the  $(3_14_1/2_14_25_1)$  dyad.

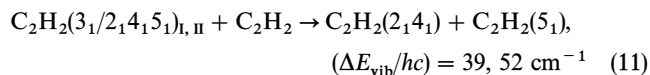
The rate coefficients for intradyad transfer induced by collisions with  $H_2$  and  $N_2$  are also reported in Table 4. As already pointed out, they mirror the trend observed for self-relaxation, in that this process is much faster within the  $(3_1/2_14_15_1)$  dyad. It seems that the factor which is responsible for this difference is independent of collision partner. Unlike the rates for vibrational relaxation which are discussed shortly, those for intradyad transfer exhibit little dependence on the collisional reduced mass, suggesting that the process cannot be governed solely by short range repulsive forces as assumed in the theory of Schwarz, Slawsky and Herzfeld (SSH).<sup>1</sup> Consequently, it seems that long-range attractive forces may be important, not only in self-relaxation, but in the case of other collision partners.

Table 4 also records the rate coefficients for vibrational relaxation from the two pairs of coupled Fermi dyad states  $(3_1/2_14_15_1)$  and  $(3_14_1/2_14_25_1)$ . It is useful to compare these

results with those of previously related studies and to consider the reasons that might lead to (a) the relatively minor differences between the rate coefficients for relaxation from  $(3_1/2_14_15_1)$  and  $(3_14_1/2_14_25_1)$ , and (b) the strong dependence of the rate coefficients on collision partner.

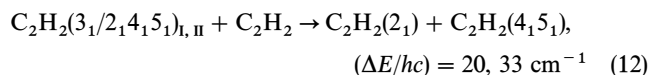
Self-relaxation, *i.e.* that of excited  $C_2H_2$  molecules by collision with other  $C_2H_2$  molecules, has been studied most extensively in the past and the results of these measurements are summarised in Table 2. Our value of  $k_{vr}$  for relaxation of  $C_2H_2$  from  $(3_1/2_14_15_1)$  can be compared most directly with the two values obtained in previous experiments in our laboratory: (a)  $(7.4 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by Smith and Warr<sup>13</sup> using the laser-induced vibrational fluorescence method, and (b)  $(7.0 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  determined in IRUVDR experiments of the kind that are described in the present paper. At  $(1.0 \pm 0.1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , our value exceeds the earlier values by a difference slightly greater than the combined random error limits but not by enough to give serious cause for concern.

Our value for the rate coefficient implies relaxation occurs once in four collisions and this high probability, which is also found for most other vibrational levels of  $C_2H_2$  above the lowest excited states (*i.e.*,  $4_1$  and  $5_1$ ) is usually interpreted as evidence for facile intermolecular vibration-to-vibration (V–V) processes that are nearly resonant. If this explanation is correct, it is important to note the importance of the Fermi resonance in facilitating intermolecular V–V relaxation *via* pathways such as:



since both molecules, in effect, undergo single quantum transitions. If, on the other hand, the excited  $C_2H_2$  molecule was in a pure  $|3_1\rangle$  state, the vibrational matrix element for the process corresponding to (11) would be much less. It is the supposition that the dominant term in the transition matrix element is that involving the  $|2_1(4_15_1)^0\rangle$  zero order state (or similar terms in the case of transfer out of the higher Fermi dyad) which underpins our assumption that relaxation from each component states of a given Fermi dyad will occur at essentially the same rate.

The V–V pathway represented by eqn. (11) was the one favoured by Frost and Smith<sup>16</sup> to explain the fast rate of self-relaxation of  $C_2H_2(3_1/2_14_15_1)$ . Their reasoning was that the high collisional probability for relaxation implied a dominant V–V process probably induced by long-range forces of the kind originally invoked by Sharma and Brau<sup>44</sup> to treat near-resonant energy transfer between  $CO_2$  and  $N_2$ . If this were so, then one would expect the most facile transfers to be those corresponding to infrared transitions in each molecule. Exchange of a  $\nu_5$  quantum in eqn. (11) satisfies this condition. The other such near-resonant process is



The matrix element for the  $(4_15_1 \leftrightarrow 0)$  transition in  $C_2H_2$  is known to be large. Other transitions, *e.g.* those involving exchange of  $\nu_2$  or  $\nu_4$  quanta, are also near-resonant but most of them involve quadrupole–quadrupole coupling on the basis of the theory of Sharma and Brau.<sup>44</sup>

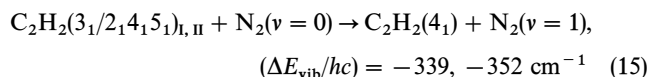
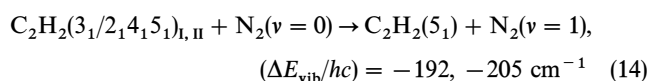
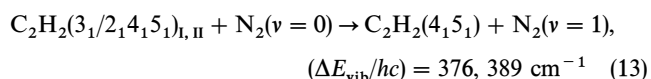
Like Frost and Smith,<sup>16</sup> we have attempted to identify relaxation pathways, in our case from the  $(3_14_1/2_14_25_1)$  dyad, and to measure the rates of relaxation from collisionally populated levels of intermediate energy by (a) recording LIF spectra at delay times corresponding to partial relaxation, and then (b) by recording kinetic traces of LIF signal *vs.* time for some of the levels thus identified. The results of these experiments are described in the next section and further discussion of the possible mechanisms for self-relaxation of  $C_2H_2$  from



the the  $(3_1/2_14_15_1)$  and  $(3_14_1/2_14_25_1)$  levels is postponed to end of that section. However, we do note here that the difference in the rate coefficients for self-relaxation from each of these Fermi dyads is quite slight suggesting that similar mechanisms are probably active in both cases.

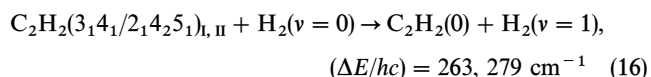
To assess the importance of the internal motions (rotations and vibrations) of the collision partners  $H_2$  and  $N_2$ , it is useful to compare the rate coefficients for relaxation by these species with the data obtained by Smith and Warr<sup>13</sup> for the relaxation of  $(3_1/2_14_15_1)$  by the noble gases. This comparison allows one to compare the difference between the measured rate coefficients for relaxation, expressed in Fig. 7 as collisional probabilities, with the values which would be expected for hypothetical atoms of mass 2 and 28 u. The data displayed in Fig. 7 show that both  $H_2$  and  $N_2$  relax the Fermi dyad levels faster than would be expected on this basis.

In the case of  $N_2$ , it is reasonable to look for the participation of intermolecular V–V exchange pathways. There are three such processes, of similar energy discrepancy, which for the case of  $(3_1/2_14_15_1)$  can be written as



Only the last of these processes involves a transition in  $C_2H_2$  which is infrared active and which could therefore involve dipole–quadrupole coupling. It is impossible to say which if any of these processes is dominant. Indeed it seems possible that all three play some role in the relaxation.  $C_2H_2$  in the  $(3_14_1/2_14_25_1)$  dyad is relaxed by  $N_2$  at only about half the rate of those in  $(3_1/2_14_15_1)$ . Although the values of  $\Delta E$  for the processes for  $C_2H_2(3_14_1/2_14_25_1)$  which are similar to processes (13)–(15) change only slightly, this information does not help with the assignment of the V–V processes responsible for the observed rate of relaxation.

With  $H_2$ , the rates of relaxation from  $(3_1/2_14_15_1)$  and  $(3_14_1/2_14_25_1)$  are essentially the same. This makes it unlikely that the V–V process



plays any significant role in relaxing  $C_2H_2$  from the upper Fermi dyad, since the equivalent process for the lower dyad

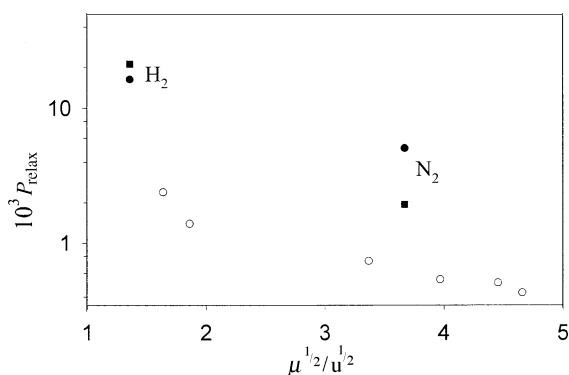
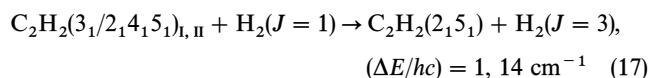


Fig. 7 Collisional transfer probabilities for vibrational relaxation vs. the square root of the collisional reduced mass. The filled circles are for the relaxation of  $C_2H_2(3_1/2_14_15_1)$  by  $H_2$  and  $N_2$ ; the filled squares are for the relaxation of  $C_2H_2(3_14_1/2_14_25_1)$  by  $H_2$  and  $N_2$ . The open circles are data for the relaxation of  $C_2H_2(3_1/2_14_15_1)$  by noble gases from Smith and Warr.<sup>13</sup>

would be ca.  $870 \text{ cm}^{-1}$  endothermic. It seems likely, however, that relaxation by  $H_2$  is accelerated by vibration-to-rotation (V–R) effects such as



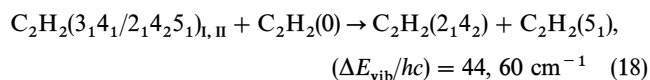
Such near-resonant channels exist for both  $H_2(J=1)$  and  $H_2(J=0)$  which contain 67% of the  $H_2$  molecules in a thermal sample at 295 K.

### (c) Spectroscopic and kinetic experiments on vibrational states formed in the collisional relaxation of $C_2H_2(3_14_1/2_14_25_1)$

In principle, double resonance techniques make it possible to identify the pathways of vibrational relaxation by observing the states which are formed following collisional relaxation of the state which is populated directly by the pumping process, in the present experiments by absorption of IR radiation. In practice, the application and interpretation of such experiments is far from straightforward. It is necessary to struggle with spectral congestion and even when spectral features are unequivocally identified interpretative difficulties remain. First, it is hard to relate intensities to populations, and hence estimate branching ratios, because of the difficulty of calculating Franck–Condon factors, especially in the presence of strong perturbations in both electronic states. Secondly, it is not always obvious how to relate the observed variation with time of the LIF signal from a particular state to the rates of formation into and loss from that particular state. Finally, if the rate of removal is appreciably larger than the rate of production, then the concentration within the level being monitored may never reach a level that can be observed.

These difficulties beset the present experiments, as they did those of Frost and Smith.<sup>16</sup> They observed populations in the  $(2_14_1)$  and  $(4_2)$  levels, as well as in a level assigned tentatively as  $(4_15_2)$ , and they determined rate coefficients for self-relaxation from these levels by performing kinetic experiments in which LIF signals were recorded at different delays between the pump and probe lasers. They suggested that the process represented by eqn. (11) which creates  $C_2H_2(2_14_1)$  might reasonably be the principal mechanism for the self-relaxation of  $C_2H_2(3_1/2_14_15_1)_{I,II}$  since it involves the exchange of a  $v_5$  quantum and can therefore occur under the influence of long range dipole–dipole intermolecular forces, in keeping with the theory propounded by Sharma and Brau.<sup>44</sup>

With this background, our first spectroscopic efforts were focused on observing  $C_2H_2(2_14_2)$  formed in the relaxation from  $(3_14_1/2_14_25_1)_{I,II}$  in the process



To this end, the time delay between pump and probe lasers was fixed at about the vibrational self-relaxation time from  $(3_14_1/2_14_25_1)_{I,II}$  and the frequency of the probe laser was scanned through the wavelength region of the  $\tilde{A}(3_1) \leftarrow \tilde{X}(2_14_2)$  and  $\tilde{A}(3_2) \rightarrow \tilde{X}(2_14_2)$  bands. No lines attributable to these bands were observed, leading us to the unexpected conclusion that the intermolecular V–V exchange processes represented by (18) are not a major pathway for relaxation from  $(3_14_1/2_14_25_1)_{I,II}$ . In the search for other collisionally populated states, several experiments of the kind that has just been described were carried out. A search for population in the  $(3_1/2_14_15_1)$  dyad via the  $\tilde{A}(3_14_1/3_16_1) \leftarrow \tilde{X}(3_1/2_14_15_1)_{I,II}$  bands, used to observe the states of this dyad when they were accessed directly by optical pumping, was unsuccessful. However, we did detect collisional population of three vibrational states:  $(2_14_1)$ ,  $(4_25_1)$  and  $(4_2)$ . The bands used to observe  $C_2H_2$  in these levels are given in Table 5.

In the case of  $C_2H_2(4_2)$ , the intensities of the LIF signals

**Table 5** Observations and rate coefficients for self-relaxation from levels populated by collisions following the excitation of  $C_2H_2(3_14_1/2_14_25_1)_{II}$

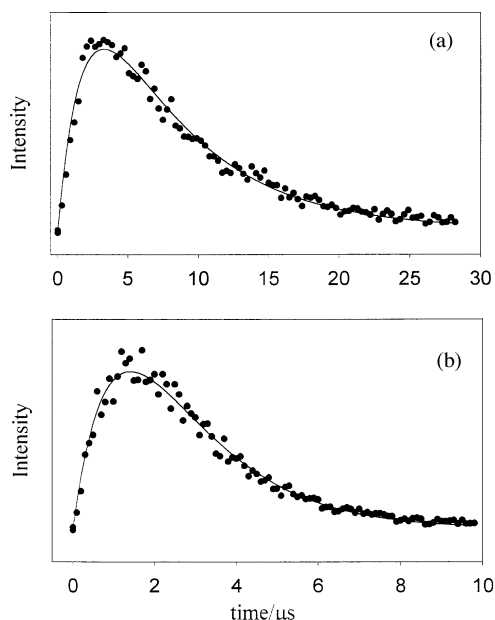
Level	Band observed	Wavelength/nm	$k/cm^3 \text{ molecule}^{-1} s^{-1}$
$4_25_1$	$\tilde{A}(4_1)^1 \leftarrow \tilde{X}(4_25_1)^1$	243.8–244.2	$(7.9 \pm 3.2)^a \times 10^{-11}$
$2_14_1$	$\tilde{A}(3_1)^0 \leftarrow \tilde{X}(2_14_1)^1$	245.5–245.9	$(2.9 \pm 0.6) \times 10^{-11}$
$4_2$	$\tilde{A}(0)^1 \leftarrow \tilde{X}(4_2)^0$	243.8–244.2	

<sup>a</sup> Errors are cited at the  $2\sigma$  level including only random errors.

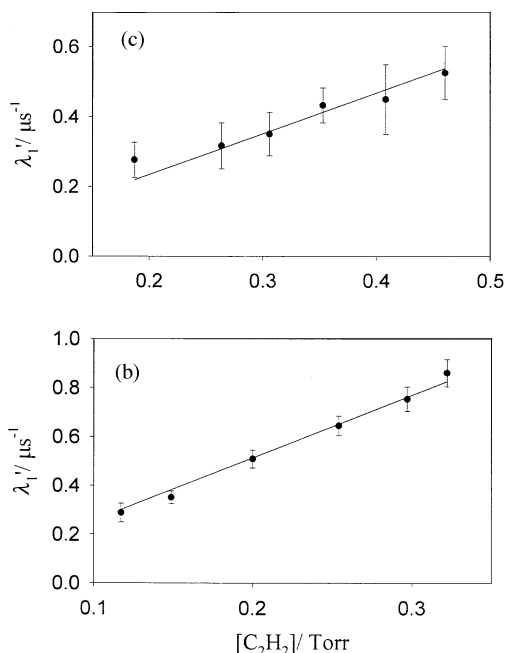
were only slightly increased when the IR pump laser was operating over those which could be recorded, in the absence of this laser, from the fraction of  $C_2H_2$  molecules present in this level in a thermal sample. Because of this, and because it was not clear that this level was populated in one collisional step from  $(3_14_1/2_14_25_1)$ , no attempt was made to record kinetic traces of LIF signal *vs.* time from this level.

However, in the case of the  $(2_14_1)$  and  $(4_25_1)$  levels, kinetic traces were recorded by fixing the frequency to a strong line in the UV bands used to observe these states and observing the variation of the LIF intensities as the delay between IR pump and UV probe was varied. The results of typical experiments are shown in Fig. 8. Such traces were fitted to a form related to that given in eqn. (3). Here  $\lambda_1$  and  $\lambda_2$  correspond to the pseudo-first-order rate coefficients for formation and removal of molecules in the observed levels, although it is not, of course, obvious which process  $\lambda_1$  and  $\lambda_2$  should be assigned to. In the case of  $(2_14_1)$ , the values of  $\lambda_1$  determining the rate of rise in the signals, corresponded to those expected for loss of population from  $(3_14_1/2_14_25_1)$  and were assigned accordingly. The values of  $\lambda_2$  were observed at different concentrations of  $C_2H_2$  [see Fig. 9(a)] yielding the rate coefficient for self-relaxation of  $C_2H_2(2_14_1)$  given in Table 5. It agrees very well with the value determined previously by Frost and Smith.<sup>16</sup>

Similar experiments were performed on  $C_2H_2(4_25_1)$ . In this case, as indicated by the trace displayed in Fig. 8(b), the values of  $\lambda_1$  and  $\lambda_2$  were similar, and close to that which was expected on the basis of one of them corresponding to relaxation from  $(3_14_1/2_14_25_1)$ . Accordingly, in analysing these traces, one first-order rate coefficient was set to the value corresponding to  $k_1 = 6.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$  that had been determined for self-relaxation from  $(3_14_1/2_14_25_1)$ . The



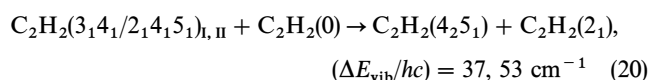
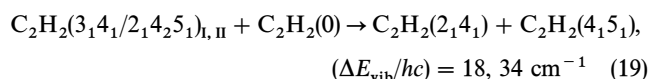
**Fig. 8** Traces of LIF signal *vs.* time from samples of pure acetylene: (a) 153 mTorr  $C_2H_2$ , exciting  $(3_14_1/2_14_25_1)_{II}$ , observing  $(2_14_1)$ ; (b) 254 mTorr  $C_2H_2$ , exciting  $(3_14_1/2_14_25_1)_{II}$ , observing  $(4_25_1)$ .



**Fig. 9** Plots of first-order constants *vs.*  $[C_2H_2]$  for: (a) decay from the  $(2_14_1)$  level, and (b) removal from the  $(4_25_1)$  level, the second first-order rate constants having been fixed to correspond to that for relaxation from  $(3_14_1/2_14_25_1)$ . In each case, allowance is made for the effects of diffusive loss.

values of the other first-order rate constant are plotted against  $[C_2H_2]$  in Fig. 9(b) and yield the rate coefficient of self-relaxation from  $(4_25_1)$  given in Table 5.

The experimental results that we have just reported suggest that the processes



play some role in the self-relaxation of  $C_2H_2$  from the  $(3_14_1/2_14_25_1)$  dyad, although we are unable to estimate branching ratios from our observations.

It is surprising that the process involving exchange of one  $\nu_5$  quantum and represented by eqn. (18) is unimportant whereas it apparently occurs easily in the relaxation from the  $(3_1/2_14_25_1)$  dyad. The reason for this difference must lie in differences in the matrix elements for collisional relaxation in the two cases and probably in differences in the wavefunctions of the pairs of states in the two Fermi dyads. In the case of  $(3_1/2_14_25_1)$ , the wavefunctions of the eigenstates are approximately equal mixtures of the zero order states  $|3_1\rangle$  and  $|2_1(4_15_1)^0\rangle$  with significant contributions from  $|2_1(4_15_1)^2\rangle$  only above about  $J = 20$ . With  $(3_14_1/2_14_25_1)$ , however, there are unequal but significant contributions from both  $|2_1(4_25_1)^1\rangle$  and  $|2_1(4_25_1)^1\rangle$ . It appears that in the matrix elements for transfer from  $(3_14_1/2_14_25_1)$  to  $(2_14_2)$  some cancellation of terms may occur that could lower the probability of this process.

## Summary and conclusions

Using an IRUVDR technique, we have measured rate coefficients for collisional relaxation of  $C_2H_2$  between component states of the two Fermi dyads  $(3_1/2_14_25_1)$  and  $(3_14_1/2_14_25_1)$  and for relaxation from these Fermi dyads. As well as self-relaxation, *i.e.* relaxation in  $C_2H_2$ – $C_2H_2$  collisions, we have determined the rates of energy transfer in collisions with  $N_2$

and H<sub>2</sub>. Finally, rate coefficients are reported for self-relaxation from two states, (4<sub>2</sub>5<sub>1</sub>) and (2<sub>1</sub>4<sub>1</sub>), that are not pumped directly but which are populated during relaxation from (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>).

With all three collision partners transfer between the component states of the (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>) dyad is several times faster than that between the components of (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>), a finding which is taken to reflect differences in the cancellation of the diagonal terms in the matrix elements for the two intradyad transitions. The difference in the efficiency of C<sub>2</sub>H<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> in inducing intradyad relaxation, with the collisional probabilities for N<sub>2</sub> and H<sub>2</sub> about an order-of-magnitude below that for C<sub>2</sub>H<sub>2</sub>, presumably indicates differences in the interaction potentials for these three collision partners.

Vibrational self-relaxation from all of the levels that have been investigated is found to be facile, with collisional probabilities ≥0.1, which probably reflects the multiple opportunities for intermolecular V–V energy transfer in such collisions. The rates at which N<sub>2</sub> and H<sub>2</sub> relax (3<sub>1</sub>/2<sub>1</sub>4<sub>1</sub>5<sub>1</sub>) and (3<sub>1</sub>4<sub>1</sub>/2<sub>1</sub>4<sub>2</sub>5<sub>1</sub>) are all greater than expected on the basis of a comparison with data for the noble gases as collisional relaxants. This observation suggests that the internal degrees of freedom in N<sub>2</sub> and H<sub>2</sub> play some part in their role as relaxants. It is suggested that V–V processes may serve to accelerate relaxation in C<sub>2</sub>H<sub>2</sub>–N<sub>2</sub> collisions, whereas V–R energy transfer may assist relaxation in C<sub>2</sub>H<sub>2</sub>–H<sub>2</sub> collisions.

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