# Vibrational excitation of *cis*- and *trans*-1, 2-difluoroethenes by electron impact: effect of dipole moment on the threshold peaks

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**Abstract**
Vibrational excitation near threshold was measured in *cis*- and *trans*-difluoroethene with the aim of assessing the role of the dipole moment in threshold peaks. Threshold peaks were found in both the isomer with and the isomer without a permanent dipole moment, but only for IR-active vibrations. A comparison with cross sections calculated with the Born approximation revealed that a 'nontrivial' contribution to the threshold peaks, that is, one which cannot be explained by direct dipole excitation, is found only for the isomer with a permanent dipole moment (*cis*).

## 1. Introduction

Threshold peaks in vibrational excitation of molecules by electron impact, discovered more than 25 years ago by Rohr and Linder (1975, 1976) in hydrogen halides, are large enhancements of cross sections in a narrow region above threshold. They are not associated with either of the common mechanisms of vibrational cross section enhancement, which are shape resonances and direct dipolar excitation of infrared-active vibrations. The latter is active predominantly near threshold and in the forward direction. Threshold peaks have been subject to deeper studies recently (Allan *et al* 2000, Čížek *et al* 2001), by taking advantage of improved experimental techniques which permitted measurements of the cross sections with higher accuracy as far as their shape near threshold is concerned and at higher resolution, revealing details of various narrow structures near threshold. Advances in theory, describing scattering in terms of a nonlocal complex potential, succeeded spectacularly in describing the shapes of the cross sections and the various narrow structures. The absence of threshold peaks has been predicted theoretically by Horáček *et al* (1997) in HI, where the dissociative attachment threshold lies below the zero of the incident electron energy scale. The prediction was confirmed experimentally by Sergenton and Allan (2000).

The threshold peaks were found in polar molecules, where the dipole moment plays an important role by binding (together with the polarization potential) the electron at large
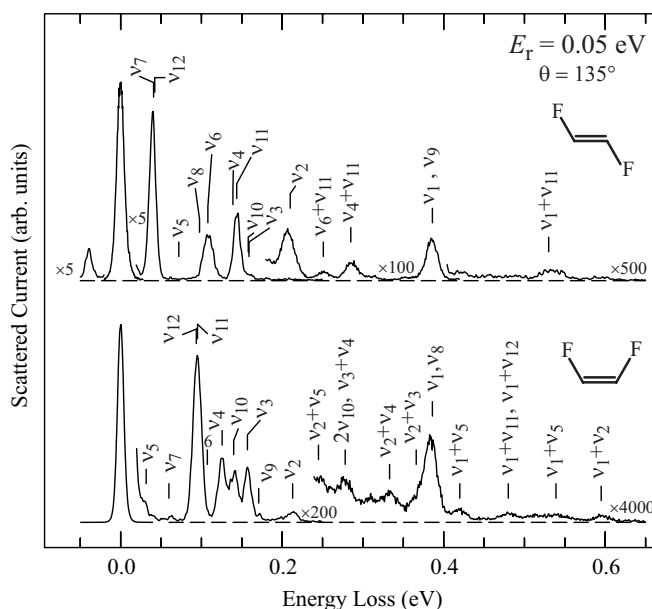
**Figure 1.** Electron energy loss spectra recorded close to the excitation threshold, with a scattered electron energy $E_r = 50$ meV. Vibrational frequencies are marked by vertical lines and labels.

internuclear distances. This bound section of the potential is decisive for the threshold peaks. The threshold peaks were also found in apolar molecules, however. The most studied example is $CO_2$, where the threshold peak, notably in the symmetric stretch vibration (more precisely in one of the Fermi-coupled vibrational states containing the symmetric stretch, Allan 2001), has been ascribed to a virtual state of the anion (Estrada and Domcke 1985, Kochem *et al* 1985, Morgan 1998).

In the present contribution we investigate how a permanent dipole moment influences threshold peaks by studying electron scattering in the two isomers of 1, 2-difluoroethene, which are chemically very similar except that the *cis* isomer has a substantial dipole moment, 2.42 D (Laurie 1961), whereas the *trans* isomer has no permanent dipole moment by symmetry. The measurements were made at the large scattering angle of 135° to minimize the direct dipolar excitation of infrared-active vibrations and thus to reveal the true threshold peaks.

## 2. Experiment

The measurements were performed using a spectrometer with hemispherical analysers described by Allan (1992, 1995). The response function of the spectrometer at very low energies has recently been improved by adding more degrees of freedom in compensating residual electric fields in the collision region, a by-product of the recently installed (Allan 2000) 'magnetic angle changer'. The resolution of the instrument in the energy-loss mode, determined on the elastic peak of helium, was 17 meV fwhm. The spectra in figure 1 at energy losses up to 0.25 eV were recorded with a resolution of 10 meV. The relatively small amount of sample available—all measurements have been made with about 0.5 g of each sample— required that the spectrometer is operated with less resolution but with higher sensitivity. The energy of the incident beam was calibrated on the 19.366 eV $^2$S resonance in helium and is

**Table 1.** Dipole moment $\mu$ (*cis* isomer, Laurie 1961), experimental vibrational energies $E$ (meV; Craig and Overend 1969, Shimanouchi 1972, NIST Web page http://webbook.nist.gov/chemistry/) and infrared intensities $A$ (Kagel *et al* 1983, 1984) of *cis*- and *trans*-difluoroethene, ordered according to the principal type of vibration.

| Type | | *cis*-difluoroethene $\mu = 2.42$ D | | | | *trans*-difluoroethene $\mu = 0$ D | | |
| | No | Sym. | $E$ | $A$ (km mol$^{-1}$) | No | Sym. | $E$ | $A$ (km mol$^{-1}$) |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| CH stretch | $\nu_1$ | $a_1$ | 389 | $3.7 \pm 3.7$[a] | $\nu_1$ | $a_g$ | 386 | 0 |
| | $\nu_8$ | $b_1$ | 389 | $3.7 \pm 3.7$[a] | $\nu_9$ | $b_u$ | 386 | $9.5 \pm 0.2$ |
| CC stretch | $\nu_2$ | $a_1$ | 213 | $42.0 \pm 0.6$ | $\nu_2$ | $a_g$ | 210 | 0 |
| CF stretch | $\nu_4$ | $a_1$ | 126 | $50.7 \pm 0.7$ | $\nu_4$ | $a_g$ | 139 | 0 |
| | $\nu_{10}$ | $b_1$ | 140 | $84.9 \pm 1.2$ | $\nu_{11}$ | $b_u$ | 144 | $217.7 \pm 4.4$ |
| CH bend | $\nu_3$ | $a_1$ | 157 | $29.4 \pm 0.5$ | $\nu_3$ | $a_g$ | 159 | 0 |
| | $\nu_6$ | $a_2$ | 107 | 0 | $\nu_6$ | $a_u$ | 108 | $56.7 \pm 0.7$ |
| | $\nu_9$ | $b_1$ | 171 | $20.0 \pm 0.4$ | $\nu_{10}$ | $b_u$ | 158 | $14.7 \pm 0.2$ |
| | $\nu_{12}$ | $b_2$ | 94 | $29.6 \pm 15$[a] | $\nu_8$ | $b_g$ | 98 | 0 |
| CCF deform | $\nu_{11}$ | $b_1$ | 95 | $30.1 \pm 15$[a] | $\nu_5$ | $a_g$ | 72 | 0 |
| | $\nu_5$ | $a_1$ | 32 | $1.8 \pm 0.1$ | $\nu_{12}$ | $b_u$ | 42 | $1.5 \pm 1.5$ |
| torsion | $\nu_7$ | $a_2$ | 60 | 0 | $\nu_7$ | $a_u$ | 41 | $12.7 \pm 1.4$ |

[a] Vibrations in the pairs $\nu_1/\nu_8$ and $\nu_{11}/\nu_{12}$ overlap, permitting only measurements of the sums of intensities.

accurate to within $\pm 30$ meV. The analyser response function was determined on the elastic scattering in helium. Absolute values of the cross sections were determined by comparison with the elastic cross section of helium of Nesbet (1979) using the relative flow method (Nickel *et al* 1989) and are accurate within about a factor of 1.5 in the first 200 meV above threshold, $\pm 30\%$ at higher energies. The reliability of the comparison between the *cis* and *trans* isomers is better than the reliability of the absolute values, however, because *cis* and *trans* isomers were measured alternately to assure that the same response function applied to both. The sample inlet nozzle had a diameter of 0.25 mm and was kept at $40\,^\circ$C during the measurements.

The commercial sample of 1, 2-difluoroethylene, which was purchased 23 years ago from PCR, Gainesville, FL, and is no longer available, was rich in the *trans* isomer. The *cis* content was increased by iodine-catalysed isomerization for 24 h at $200\,^\circ$C as described by Craig and Entemann (1961). Iodine was removed by several distillations over copper turnings. The isomers were separated by preparative gas chromatography at $0\,^\circ$C on a 4 m column packed with dibutylphthalate-coated Chromosorb. Relative elution times were 2.8 (*cis*) and 1.0 (*trans*) with almost quantitative separation. Samples of each isomer were passed through a column packed with 8–20-mesh Ascarite II (Thomas, Swedesboro, NJ) to remove residual carbon dioxide and finally dried by distillation through a column containing phosphorus pentoxide. Purities were checked by infrared spectroscopy (Craig and Overend 1969). For the *trans* isomer, *cis* was less than 0.5%; for the *cis* isomer, *trans* was less than 1.0%.

## 3. Results

Vibrational frequencies have been summarized in table 1, grouped according to the principal type of motion involved. The energy loss spectra shown in figure 1 have been recorded by collecting scattered electrons with a fixed residual energy of $E_r = 0.05$ eV and varying the incident electron energy. All the bands were thus recorded 0.05 eV above their respective excitation thresholds—the spectra are indicative of vibrations excited strongly at threshold. The spectra reveal a correlation between the threshold intensity and the infrared
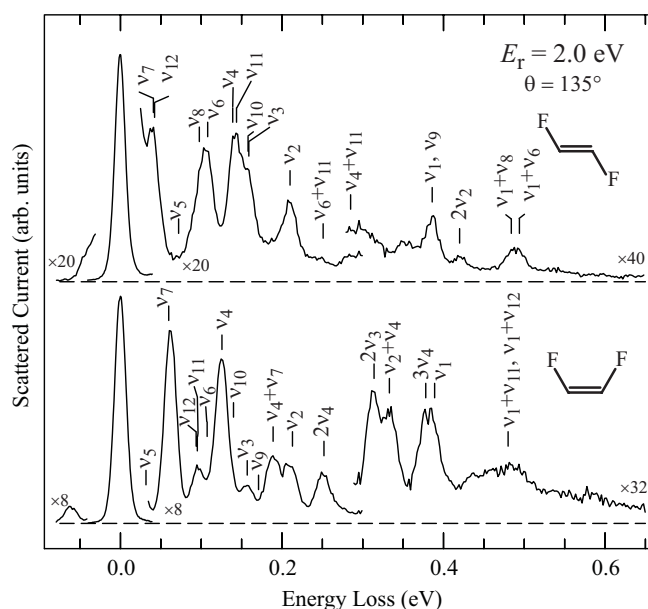
**Figure 2.** Electron energy loss spectra recorded with a scattered electron energy $E_r = 2$ eV, that is, within the $\pi^*$ resonance region. Vibrational frequencies are marked.

intensity. The vibrations which are inactive or weak in the IR, for example $\nu_5$, $\nu_{10}$ and $\nu_3$ in *trans*-difluoroethene and $\nu_7$ in *cis*-difluoroethene, are generally weak in the threshold spectra. The spectra are dominated by vibrations with large IR intensities. Overtone and combination vibrations are very weak.

The energy loss spectra shown in figure 2 have been recorded within the $\pi^*$ shape resonance region, by collecting scattered electrons with a fixed residual energy of $E_r = 2$ eV. The selectivity of the excitation is given by the antibonding properties of the $\pi^*$ molecular orbital (MO). This MO is nominally antibonding with respect to the C=C bond, but extends also to the fluorine atoms, explaining the high intensity of the C–F stretch vibrations, $\nu_4$ in *cis*-difluoroethene and (unresolved) $\nu_4$ and $\nu_{11}$ in *trans*-difluoroethene. The C=C stretch vibration $\nu_2$ is clearly excited in both molecules. The torsion vibrations $\nu_7$ are strongly excited in both molecules by vibronic coupling of the $\pi^*$ and the $\sigma^*_{C-F}$ resonances. Note that in the resonance region vibrations of the same type, for example the C=C stretch vibrations $\nu_2$, the C–F stretch vibrations $\nu_4$ and the torsion vibrations $\nu_7$, are excited to the same degree in both isomers as expected. There is one exception to this rule, however: the C–H out-of-plane bend vibrations $\nu_6$ and $\nu_8$ are strongly excited in the *trans* isomer, but their counterparts $\nu_6$ and $\nu_{12}$ in the *cis* isomer are excited only weakly. Finally, combination and overtone vibrations can be discerned in several instances in the spectra in figure 2—characteristic of excitation via a shape resonance.

Figure 3 shows the elastic cross sections. The size of the elastic cross section is strongly enhanced at low energies by the permanent dipole moment of *cis*-difluoroethene, as expected. The large elastic cross section of *cis*-difluoroethene at low energies has a practical consequence for the measurements: it enhances double scattering of slow electrons, and suppresses threshold peaks at higher pressures. As with the hydrogen halides, it is therefore essential to measure at very low pressures.

Figures 4 and 5 compare the cross sections of the C=C stretch and the C–F stretch vibrations for the two isomers. A band due to the $\pi^*$ shape resonance is seen for both types
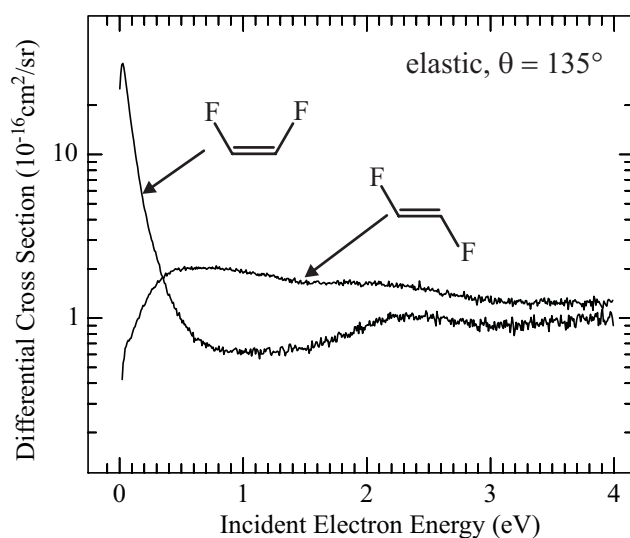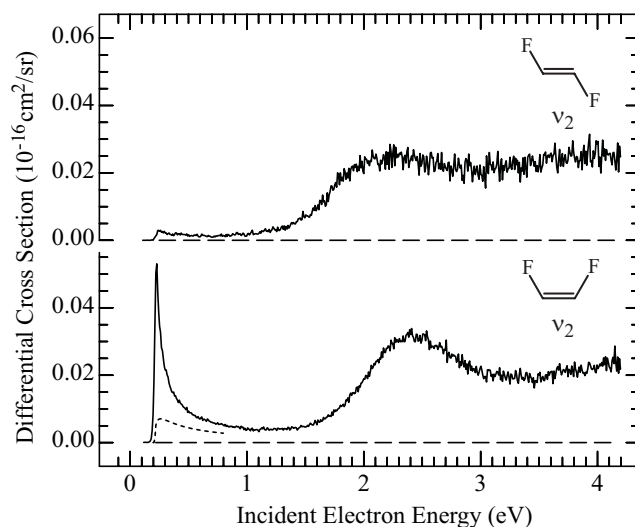
**Figure 3.** Elastic cross sections.



**Figure 4.** Cross sections for the excitation of the C=C stretch vibrations $\nu_2$. The dashed curve is the cross section calculated from the infrared intensities using the Born approximation.

of vibration, yielding vertical electron attachment energies of 2.37 eV for *cis*-difluoroethene and 2.05 eV for *trans*-difluoroethene. The resonances thus lie slightly higher than in the parent compound ethene, which has a resonance at 1.78 eV (Jordan and Burrow 1978). The effect of the fluorine substituents may be viewed as a stabilizing inductive effect due to the large electronegativity of fluorine and a destabilizing conjugative effect due to admixture of the occupied lone pair orbitals of $\pi$ symmetry on the fluorines. The higher energy of the resonance in the *cis*-compound can be visualized within this picture as due to destabilizing through-space interaction of the fluorine lone pairs of $\pi$ symmetry.

Vertical electron attachment energies can be estimated from Hartree–Fock (HF) virtual MO energies, using Koopmans' theorem with empirical scaling (Howard and Staley 1984,
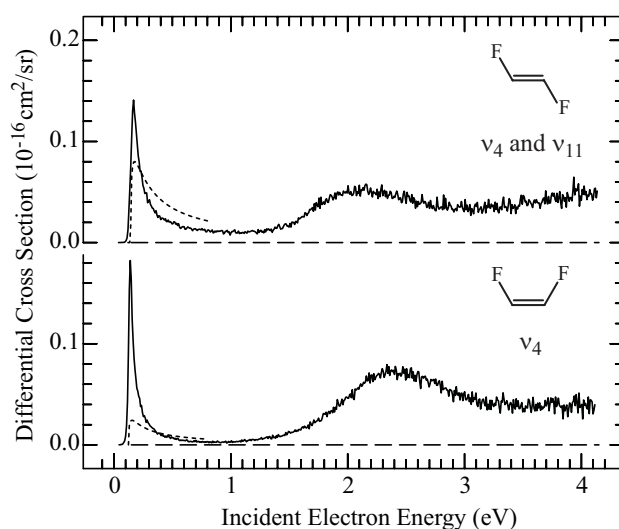
**Figure 5.** Cross sections for the excitation of the C–F stretch vibrations $\nu_4$ in *cis*-difluoroethene and overlapping $\nu_4$ and $\nu_{11}$ in *trans*-difluoroethene. Born cross sections are shown dashed.

Heinrich *et al* 1986, Chen and Gallup 1990). Our experience with many compounds has shown that this method is reliable within ±0.3–0.5 eV and works well with either the 6-31G or the 6-31G* basis sets. With the present compounds the result depends sensitively on which of the two basis sets is used, however, and a satisfactory result was obtained only with the larger one. The 6-31G* basis set with the scaling parameters of Chen and Gallup (1990) and at the HF/6-31G* optimized geometry yielded 2.24 and 2.17 eV for the *cis* and *trans* isomers, respectively, in good agreement with the observation. The agreement with the experiment did not improve when the experimental geometries of Craig *et al* (1996) were used.

The cross sections retain substantial values even above 3 eV, presumably because of two $\sigma_{C-F}^*$ resonances, predicted to lie around 3.5 and 4 eV in both isomers by the scaled Koopmans theorem method.

## 4. Discussion of the threshold peaks

Figure 4 shows that the C=C stretch vibrations $\nu_2$ are excited to about the same degree in the $\pi^*$ shape resonance region as expected from the C=C antibonding character of the temporarily occupied orbital. A threshold peak appears only in the *cis* isomer, however, where $\nu_2$ is IR active, and not in the *trans* isomer, where $\nu_2$ is IR inactive. Figure 5 shows a similar comparison for the C–F vibrations, although the situation is somewhat complicated by the overlap of $\nu_4$ and $\nu_{11}$ in the *trans* isomer. The C–F vibrations are excited to about the same degree in both isomers in the $\pi^*$ shape resonance region as expected from the C–F antibonding character of the temporarily occupied orbital. The vibration $\nu_4$ is IR inactive in the *trans* isomer, but the absence of a threshold peak for this vibration cannot be verified because of the overlapping IR active vibration $\nu_{11}$. The absence of a threshold peak for IR-inactive vibrations can be verified for $\nu_7$ in the *cis* isomer (figure 6). The vibration $\nu_7$ is IR active in the *trans* isomer, and a threshold peak is observed in figure 7. (The vibration $\nu_7$ overlaps with $\nu_{12}$ in the *trans* isomer, which is, however, very weak in the IR.) It thus appears that no threshold peaks are found for IR-inactive vibrations with the present compounds.
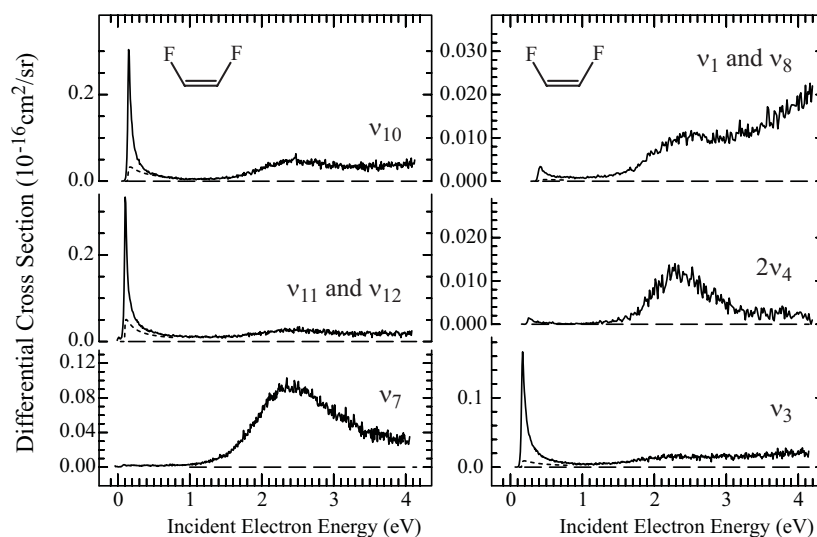
**Figure 6.** Cross sections for the excitation of various vibrations in *cis*-difluoroethene. Born cross sections are shown dashed.
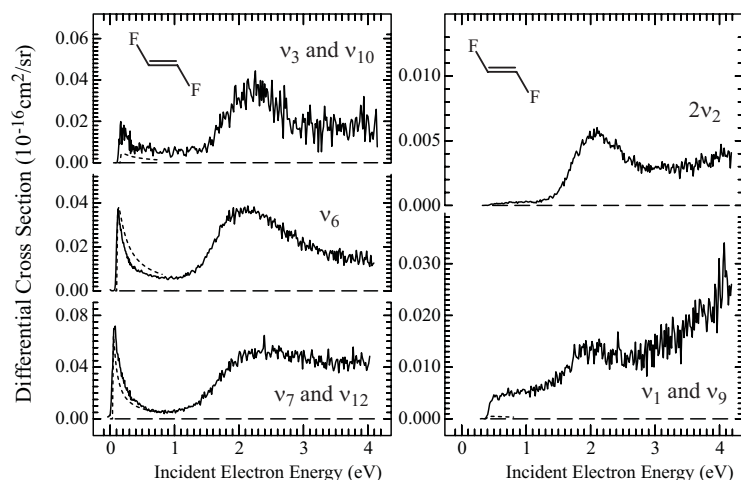


**Figure 7.** Cross sections for the excitation of various vibrations in *trans*-difluoroethene. Born cross sections are shown dashed.

Inspection of figures 4–7 reveals that the threshold peaks are generally higher, both absolutely and relatively to the height of the $\pi^*$ band, for the *cis* isomer than for the *trans* isomer. This is true for $\nu_2$, $\nu_3$, $\nu_{10}$, $\nu_{11}$ and $\nu_{12}$ of the *cis* isomer compared with $\nu_2$, $\nu_6$, $\nu_7$ and $\nu_{12}$ of the *trans* isomer, to a lesser degree for the comparison of the C–F stretch vibrations in figure 5. It thus appears that the permanent dipole moment of the *cis* isomer enhances the threshold peaks.

The question must then be addressed of whether the observed threshold peaks can be entirely attributed to the trivial mechanism of direct dipole excitation, or whether there is evidence for nontrivial threshold peaks due to dipole bound or virtual states. The present spectra were recorded at the large scattering angle of 135° to reduce the effect of direct dipole

excitation, which peaks in forward scattering, but the possibility of a contribution of the direct dipole excitation cannot be entirely discarded *a priori*, despite the large scattering angle.

We resort to the Born dipole approximation to estimate the contribution of the dipole mechanism. The range of validity of this approximation is in the near-threshold region and at low scattering angles (Takayanagi 1984), the second condition not being fulfilled in the present case. The extensive work of the Kaiserslautern group has shown that, whereas the Born dipole approximation has rather limited quantitative applicability outside the more forward-scattering angles, it can provide useful qualitative estimates even at large angles in some cases, for example for the bending mode of $CO_2$ (Kochem *et al* 1985). We compare our experiment with the Born cross sections with the expectation of gaining useful qualitative insight.

We calculated the first-order Born approximation cross sections using the the expression of Itikawa (1971) as given by Takayanagi (1984)

$$\sigma_{0\to 1} = \frac{4}{3} \sqrt{\frac{E_f}{E_i}} \frac{D^2}{(ea_0)^2} \frac{1}{K^2}$$

with

$$K^2 = \left( E_i + E_f + \sqrt{E_i E_f} \cos\theta \right) \Big/ (\mathrm{Ry} \cdot a_0^2).$$

$E_i$ and $E_f$ are the initial and final electron energies, and Ry is the Rydberg energy. We derived the squared transition matrix element from the measured infrared intensities $A$ of Kagel *et al* (1983, 1984) given in table 1 as

$$\frac{D^2}{(ea_0)^2} = \frac{A}{g\tilde{\nu}} \frac{3\varepsilon_0 hc}{2\pi^2 N_A}$$

where $g$ is the degeneracy factor, $\tilde{\nu}$ the wavenumber of the IR radiation, $N_A$ Avogadro's number and $\varepsilon_0$ the permittivity of empty space (Bishop and Cheung 1982). With $A$ in km mol$^{-1}$ and $\tilde{\nu}$ in cm$^{-1}$ this expression becomes $D^2/(ea_0)^2 = 0.0618A/g\tilde{\nu}$.

The Born approximation cross sections shown by dashed lines in figures 5–7 are based on the observed IR intensities given in table 1, but we also calculated the IR intensities using the density functional theory (DFT) at the B3LYP/6-31G* level, as implemented in the *Gaussian 98* program package (Frisch 1998). The results are very similar to those obtained with the MP2/6-31G* model by Suto *et al* (1993). The calculated intensities for the stronger bands, with intensities larger than about 30 km mol$^{-1}$, agree very well with the experiment, within about 20%. The discrepancy is larger, up to a factor of about two, for the weaker bands. The difference is even larger for the very weak band $\nu_{12}$ of *trans*-difluoroethene, with a measured intensity of 1.5 km mol$^{-1}$ and calculated intensity of 12 km mol$^{-1}$. The generally very good agreement of the calculated intensities with the experiment may be to some degree fortuitous, however, because it worsened substantially with the 6-311+G* basis set. This is in line with the conclusions reached by da Silva *et al* (1999) in their extensive study with the Møller–Plesset 2 (MP2) model.

Overlap of infrared bands allowed the measurement of only the sums of the intensities in certain cases in *cis*-difluoroethene, namely for $\nu_1$ and $\nu_8$, and for $\nu_{11}$ and $\nu_{12}$. The DFT calculation indicates that $\nu_1$ is much stronger than $\nu_8$, and $\nu_{11}$ and $\nu_{12}$ are about equally intense. A similar problem arises for the overlapping $\nu_7$ and $\nu_{12}$ of *trans*-difluoroethene. These problems do not affect the present comparison, however, because the same bands also overlap in the present energy-loss experiment. We observe the sum of the cross sections and compare it with the sum of the Born approximation cross sections in these cases.

Figures 4–7 reveal that the Born cross sections reproduce the experiment fairly well for the *trans* isomer but the measured cross sections are at least five times larger than the Born

prediction at threshold for the *cis* isomer. In view of the dramatic, qualitative nature of the observation and the fact that the behaviour is consistent for all vibrational modes for which it could be studied, we feel that the following two rules can be derived, in spite of the limitations of the Born approximation discussed above. (i) As already noted above, no appreciable threshold peaks are found for vibrations where the Born cross section is zero, that is for IR-inactive vibrations. It thus appears that a necessary condition for a threshold peak is that the dipole moment must vary as a function of the nuclear coordinate of the given normal mode. No appreciable threshold peaks are found for the (IR-inactive) overtone vibrations either. (ii) In most cases, the height of the observed peak is explained by the Born approximation cross section alone for the *trans* isomer, but the Born cross section is much less than the observed peak for the *cis* isomer. It thus appears that a permanent dipole moment is required for a 'nontrivial' contribution to the threshold peak, one which cannot be explained by the dipole mechanism alone.

The threshold peak for the overlapping $\nu_1$ and $\nu_8$ vibrations in the *cis* isomer (figure 6) is weak, but the Born cross sections are even smaller. The pattern is thus the same as for the other vibrations: the threshold peaks observed in the *cis* isomer are several times larger than the Born prediction. A very weak threshold peak is observed for the overtone vibration $2\nu_4$ of the *cis* isomer, which has only a very small IR activity. No threshold peak is observed for the IR-inactive $2\nu_2$ overtone of the *trans* isomer. The cross section near threshold for the (overlapping) C–H bend vibrations $\nu_3$ and $\nu_{10}$ of the *trans* isomer appears larger than the Born prediction in figure 7. The energy-loss spectrum in figure 1, recorded with a resolution of 10 meV, shows clearly, however, that the signal at threshold is very weak for $\nu_3$ and $\nu_{10}$, and thus does not contradict rule (ii) above. The spectra in figure 7 were recorded with a lower resolution, 17 meV, and the $\nu_3/\nu_{10}$ band overlaps partly with the $\nu_{11}$ band, causing an artifact peak at threshold in the $\nu_3/\nu_{10}$ cross section. The artifact peak has been reduced in figure 7 by subtracting some $\nu_{11}$ signal from the $\nu_3/\nu_{10}$ signal, but the result is an increased uncertainty of the $\nu_3/\nu_{10}$ cross section near threshold. The cross section for $\nu_1$ and $\nu_9$ C–H stretch vibrations in figure 7 is larger than the Born prediction at threshold. It has the shape of a step, however, not a threshold peak. This threshold signal is probably due to a $\sigma^*$ resonance extending all the way down to threshold and thus does not represent an exception to the above rule (ii) either.

## 5. Conclusions

Vibrational excitation has been found to be enhanced in two energy regions within the energy range covered by the present study. In the $\pi^*$ shape resonance region around 2 eV, the selectivity of the vibrational excitation has been found to be governed by the well known principles. These are primarily the antibonding character of the temporarily occupied $\pi^*$ orbital with respect to the C=C and C–F bond lengths, and the vibronic coupling between the $\pi^*$ shape resonance with higher-lying $\sigma^*$ shape resonances, which excites torsion vibrations.

This study is primarily concerned with the threshold peaks, which were found to obey two qualitative rules in *cis*- and *trans*-difluoroethene.

- The cross sections for IR-inactive vibrations have no threshold peaks. Variation of the dipole moment with nuclear coordinate is thus a necessary prerequisite for a threshold peak.

- A permanent dipole moment is required for the threshold peak to have a 'nontrivial' contribution, that is to be substantially higher than the prediction of the Born approximation.

## Acknowledgments

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