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σ^* resonances in electron impact-induced vibrational excitation of *n*-propane, cyclopropane, ethylene oxide, cyclopentane, and cyclohexane

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Electron-energy-loss spectra in the range of vibrational excitation, and excitation functions for selected vibrational peaks, were measured for the title compounds. Angular distributions of the vibrationally inelastic peaks were measured for *n*-propane and cyclopropane. The results in *n*-propane are similar to the published results in ethane, only one very broad band is observed in all channels, with gradual onset at about 3 eV and a maximum around 8 eV. In contrast, narrower resonances emerge in all cyclic compounds. The effect is most pronounced in cyclopropane, where two resonances appear, at 2.6 and 5.5 eV. The latter is exceptional in several respects. It is narrow and thus relatively long lived for a shape resonance of this energy. It causes ring stretch excitation with very high selectivity and pronounced angular distribution, which is reproduced very well by the theory of Read and Andrick, revealing dominance of a partial wave with an unusually high angular momentum, $l=3$, $m=3$, and unambiguously identifying the resonance as a_2' . The resonances in ethylene oxide are similar, but somewhat broader and shifted to 3 and 4.8 eV, respectively. Resonances in cyclopentane and cyclohexane resemble loosely the cyclopropane case. It is concluded that the major cause of the dramatic differences in spectral appearance between linear and cyclic alkanes are not major changes of resonant energies, but decrease of their (lifetime-determined) width, caused by higher symmetry, rigidity, and consequently larger contribution of partial waves with high l to the scattering. This implies that the vertical electron affinity of linear alkanes is not around -8 eV, as could be assumed from the position of the peak in the attachment spectra, but higher, around -3 eV. © 1996 American Institute of Physics. [S0021-9606(96)03131-5]

I. INTRODUCTION

Experimental information on σ^* valence orbitals in alkanes and related saturated organic compounds may be gained by the study of σ^* -shape resonances in electron scattering, that is of transient negative ions where the σ^* orbitals are temporarily occupied. Such investigations of σ^* resonances have traditionally been somewhat neglected in comparison to the π^* resonances.¹ The reason is primarily the large energy width of the σ^* resonances caused by their very short lifetime, often accompanied by large Franck–Condon widths of the dissociative σ^* resonances.

The large width of the σ^* -shape resonances hinders their observation in the electron transmission spectroscopy (ETS) which has been used for pioneering studies of resonances in hydrocarbons² (see also an example of ETS of *n*-pentane³). The experimentally more demanding method of recording cross sections for vibrational excitation by electron impact is more suitable for the observation of broad shape resonances since it is a “zero background” method. It has the further advantage of often giving additional evidence for the assignment of the resonances through the selectivity of the vibrational excitation and angular distribution of the scattered electrons. The latter method has been applied to alkanes larger than methane only very rarely. Boesten *et al.*⁴ have studied vibrational excitation of ethane by electron impact and has found an extremely broad band, extending from

about 4 eV to more than 15 eV, peaking at around 7 eV. The band peaks at only slightly different energies in the excitation of the different vibrations. From this result it could be concluded that σ^* resonances in alkanes have similar characteristics as the σ^* resonance in H_2 ,⁵ that is that they are exceedingly wide because of extremely short lifetime, to such a degree that it may not even be justified to view them in the chemically useful way as temporary occupation of distinct σ^* orbitals. There has been an early evidence from ETS, however, that narrower and more distinct resonances are found in cyclic alkanes.⁶ Preliminary experiments from this laboratory have shown pronounced selectivity of vibrational excitation in cyclopropane.^{7–9} The present work deepens the cyclopropane study, and presents results from related compounds, in an attempt to better characterize resonances, and indirectly σ^* orbitals, in alkanes and other saturated organic compounds.

Another technique yielding information on σ^* orbitals is the inner-shell excitation spectroscopy, which has also been applied to cyclic alkanes.^{10,11} The core is positively charged in this technique, in contrast to the neutral core in the present experiments, permitting only an indirect comparison of the results. Finally, σ^* orbitals are temporarily occupied also in the σ^* -valence excited states. Studies of these states are rare, however, such states being difficult to identify because of generally large Franck–Condon widths and extensive valence–Rydberg mixing.

II. EXPERIMENT

The instrument and the procedure of calibrating its response as a function of the incident and residual energies on helium have already been described^{12,13} and only a very brief description is given here. It is essentially a standard electron-energy-loss spectrometer using hemispherical electrostatic deflectors for electron energy selection. The analyzer can be rotated from -3° to 135° with respect to the incident beam. Sample gas was introduced into the collision region as an effusive beam through a nozzle with $250\text{ }\mu\text{m}$ diameter, kept at about 70°C . Instrumental response function for elastic scattering has been determined with help of the helium elastic signal, the analyzer response function has been determined on the helium near threshold ionization continuum. The excitation functions and energy-loss spectra were corrected for the instrumental response function, under the assumption of the product rule of the analyzer and monochromator sensitivities.¹² The present paper concentrates on excitation at higher energies, the performance of the instrument was not optimized very close (few tenths of an electronvolt) to threshold and this region is not shown in the excitation functions. The angular distribution spectra were measured by repetitively scanning the analyzer position with a stepping motor. The response function of the instrument with respect to the scattering angle has been calibrated on the helium elastic signal and the angular distribution spectra were corrected accordingly.¹³ Absolute elastic cross section in cyclopropane has been determined using the relative flow technique. The error of the absolute value is within $\pm 35\%$. The energy scale was calibrated on the 19.366 eV resonance in helium and is accurate within $\pm 30\text{ meV}$, the resolution was between 15 and 25 meV (fwhm, in energy-loss mode).

III. RESULTS AND DISCUSSION

The first part of the experimental results consists of energy-loss spectra in the range of vibrational excitation, recorded at various incident energies. This work emphasizes on resonant scattering. Large scattering angles of 90° or 120° were therefore generally chosen to reduce the contribution of direct (dipole) excitation of IR-active vibrations, which peak in the forward scattering (and at low incident energies). Vibrational excitation is generally dominated by the “shape” resonances where the incident electron may be thought of as being temporarily trapped in a normally vacant MO, without electronic excitation of the target molecule. Resonant vibrational excitation is induced by geometry relaxation during the short lifetime of the resonance, the intensities of vibrational peaks being indicative of along which normal modes did the relaxation occur. The usefulness of the vibrational intensities thus lies in the fact that they can be qualitatively related to the bonding or antibonding properties of the temporarily occupied MOs.¹⁴

The present study is concerned with relatively large molecules with many vibrations of closely spaced frequencies,¹⁵ which cannot be all resolved with the electron-impact experiment. Useful information may be derived from the spectra despite this circumstance, however, because the unresolved

vibrations of similar frequencies are generally of the same type, for example a number of C–H stretch vibrations are found around $370\text{--}380\text{ meV}$, H–C–H scissoring and deformations around 180 meV , C–C stretch vibrations around $100\text{--}110\text{ meV}$. The spectra thus indicate which type of motion is excited by a given resonance, even in cases where the exact vibration, in particular its symmetry, cannot be determined. The useful qualitative relation between antibonding properties of the temporarily occupied MO and vibrational excitation intensity may thus be used even for the present large molecules, without detailed assignment of the vibrations.

Symmetry arguments indicate that totally symmetrical vibrational modes will be excited for nondegenerate orbitals and for an electron entering and leaving the molecule in the same partial wave, and totally symmetrical vibrations are in practice generally found to dominate resonant vibrational excitation. We therefore label a given peak in the energy-loss spectrum as a totally symmetrical vibration in cases where closely spaced vibrations cause ambiguity, since the totally symmetrical vibration is likely to be responsible for a majority of the peak's intensity even when contribution of other vibrations, of different symmetry (but generally of the same type) cannot be excluded. In the case of degenerate orbitals, found in the present work in cyclopropane, vibrations with the symmetry species equal to the direct product of the species of the MO with itself may also be excited.¹⁶ Excitation of other nontotally symmetrical vibrations were also observed in previous work, and may be attributed to vibronic coupling between resonances¹⁷ or to the electron leaving in an s wave.^{16,18}

The dependence of the intensity (i.e., the relative differential cross section, DCS) of selected vibrational energy-loss peaks, previously identified in the energy-loss spectrum, is then recorded as a function of incident electron energy in the next stage of the experiment. A band in such an excitation function, indicating enhanced vibrational excitation at given incident energies, can generally be associated with a shape resonance. An attempt is then made to associate it with temporary occupation of orbitals with nodal structure and thus antibonding properties consistent with exciting the given type of vibrational motion.

The dependence of the DCS on scattering angle is also given in propane and cyclopropane, it may be indicative of the symmetry of the resonance causing the vibrational excitation.

Figure 1 shows energy-loss spectra of propane, recorded at two incident energies. Propane has 27 vibrational modes out of which nine ($\nu_1\text{--}\nu_9$) are totally symmetrical.¹⁵ They cannot all be resolved but the type of motion which is excited can generally be determined without ambiguity, because vibrations of similar type (similar local motion) tend to have similar frequencies. For example, all C–H stretch vibrations have transition energies of about 360 meV (representative symbol ν_1 is used to label the peak), H–C–H deformation vibrations about 170 meV (representative label ν_6), torsion vibrations 27 meV . The symmetrical C–C stretch ν_8 at 107 meV has a unique transition energy even with the

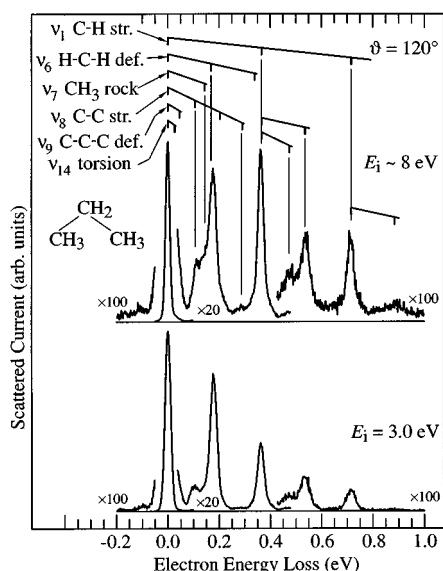


FIG. 1. Energy loss spectra of propane. (The top spectrum is a sum of spectra recorded at 7.6 and 8 eV.)

present resolution and can be unambiguously identified in the spectrum (the antisymmetrical C–C stretch ν_{20} is at 131 meV, an energy which is sufficiently different to be resolved). The intensities of the vibrationally inelastic peaks in Fig. 1 thus indicate changes (nearly certainly lengthening) of C–H bond lengths, changes of H–C–H angles, and of the C–C bond length upon an attachment of 3 or 8 eV electrons.

The most intense inelastic peak in the top spectrum of Fig. 1 is at an energy loss of 363 meV. It is wider than the elastic peak (28 meV compared to 19 meV), indicating simultaneous excitation of several totally symmetrical vibrations, presumably ν_1 , ν_2 , and ν_3 , (369, 367, and 358 meV), all of which are C–H stretch vibrations. (A less probable cause is high degree of rotational excitation.) This peak thus points, despite the ambiguity of the assignment, to lengthening of the C–H bond in the negative ion, that is to a temporary occupation of an orbital with nodes across the C–H bond. The second highest peak is at 173 meV. It is even wider than the C–H peak, and is presumably dominated by the excitation of ν_4 , ν_5 , and ν_6 , (183, 181, and 169 meV), all of which are H–C–H deformation vibrations. Other, nontotally symmetrical, vibrations in the 170–190 meV range are ν_{11} , ν_{17} , ν_{18} , and ν_{24} .¹⁵ They could also contribute to the energy-loss peak at 173 meV, but are also H–C–H deformation vibrations, so that the conclusion that attachment of an electron changes the H–C–H angle is not affected by the ambiguity of the vibrational assignment. Excitation of ν_8 (C–C stretch, 107 meV¹⁵) is clearly visible as a shoulder at 110 meV. The gap between the 110 meV shoulder and the 173 meV peak is “filled” with signal, indicating probably the excitation of ν_7 (CH₃ rock, 144 meV). There is a clear indication of the excitation of the $2\nu_1$ (and other C–H stretch) overtone and the $\nu_1 + \nu_2$ and $\nu_1 + \nu_8$ combination vibrations. Finally, the asymmetrical appearance of the elastic peak, with a tail on the right side, indicates excitation of

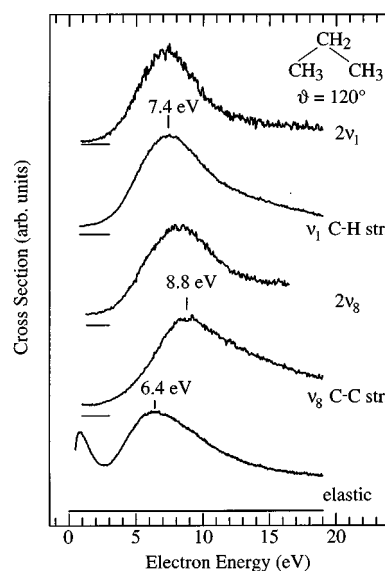


FIG. 2. Relative elastic (bottom) and vibrationally inelastic cross sections for propane, recorded as a function of the incident electron energy. The vibrational labels are only representative, other unresolved vibrations may also be excited as explained in the text.

low-frequency vibrations at 8 eV, either C–C–C deformation (ν_9) or torsion (ν_{14} or ν_{27}).

Revealing is the excitation of overtones and of combination vibrations $\nu_1 + \nu_6$ and $\nu_1 + \nu_8$, since it further supports the conclusion that the observed excitation is resonant (caused by geometry relaxation during the lifetime of the temporary anion) and not direct excitation of infrared active modes.

Figures 2 and 3 show the energy dependence of the vibrational excitation cross sections. The data is relative and the individual curves are not on the same vertical scale. The

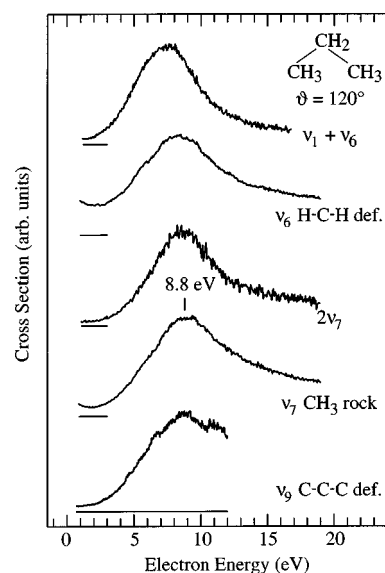


FIG. 3. Vibrationally inelastic cross sections for propane, continued from Fig. 2.

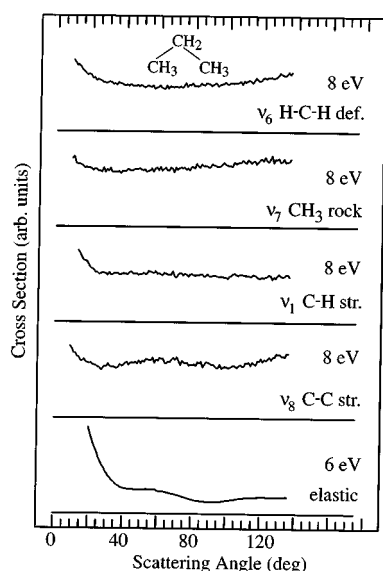


FIG. 4. Relative DCSs in propane recorded in function of the scattering angle.

elastic cross section is included for completeness in the bottom of Fig. 2. The signal does not drop to zero at low energies, but the signal remaining to the left of the broad resonance peak is probably due to direct excitation of overlapping IR-active modes, as is evidenced by the fact that the signal approaches zero much more for the excitation of the overtone $2\nu_1$ than for the excitation of the IR allowed fundamental ν_1 .

All the inelastic DCSs in Figs. 2 and 3 exhibit only a single extremely broad band with an onset at around 3 eV, and this result resembles the observation in ethane.⁴ The peak is at a slightly higher energy (8.8 eV) for the C–C excitation than for the C–H excitation (7.4 eV), and the band is broader.

Figure 4 shows the angular dependence of selected energy-loss peaks, recorded at 8 eV, near the cross section maxima (see Figs. 2 and 3). Angular dependence of the elastic cross section at 6 eV is also shown—it is not directly relevant for the present discussion, but may be a useful reference for theoretical studies. The angular distributions are not far from isotropic, without indication of the dominance of any partial wave, indicating mixture of partial waves and possibly overlapping resonances.

No distinct resonances are thus observed apart from the very broad band, and not many conclusions can be drawn from the data with respect to resonance assignment. Noteworthy is, however, that the CH_2 scissoring peak in Fig. 1 is more prominent at 3 eV than at 8 eV. This observation has an analogy for all the compound studied here as will be discussed below.

Figure 5 shows energy-loss spectra of cyclopropane. The general features resemble the propane spectra: C–H stretch, H–C–H deformation (scissoring), and C–C (ring) stretch are prominent, overtone and combination vibrations are excited. Note that the elastic peak has now symmetrical shape, cyclo-

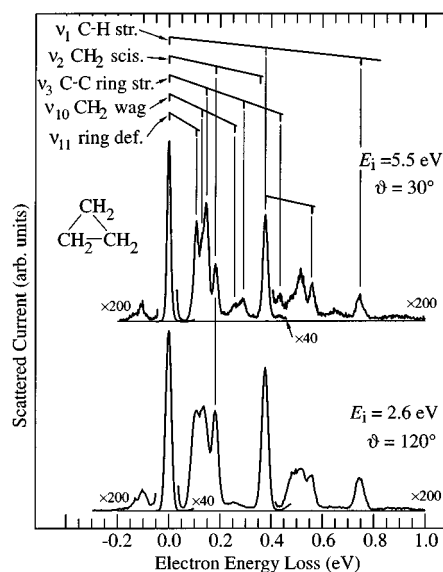


FIG. 5. Energy loss spectra of cyclopropane.

propane is rigid and does not have very low frequency deformation and torsion vibrations¹⁵ which caused a tail on the elastic peak in propane. Important for the following discussion is that the excitation of both the first and the second overtones of the ν_3 ring stretch vibration can be discerned nearly unobscured in the 5.5 eV spectrum. Cyclopropane does not have any totally symmetrical vibration which could be responsible for the peak at 108 meV, the possible assignments of this peak appear to be ν_7 , a_2'' CH_2 rock or ν_{11} , e' ring deformation. The large width of the peak at 146 meV indicates excitation of another overlapping vibration, probably the e' CH_2 wagging vibration ν_{10} (128 meV¹⁵).

An interesting detail is that the ν_1 peak is only slightly wider than the elastic peak in the upper curve of Fig. 5 (22.5 meV compared to 16.5 meV). This is probably a consequence of the fact that there is only one totally symmetrical C–H stretch vibration in cyclopropane, while there are three, spaced by 11 meV, in *n*-propane. The CH_2 scissoring peak is more prominent at the lower incident energy, as in *n*-propane.

Figure 6 shows the absolute elastic DCS, which represents an important reference for theoretical calculations. (Angular dependence of the absolute elastic DCS have already been shown and compared to existing calculations in Ref. 9). Relevant for the present discussion is that the broad 6 eV peak in the elastic DCS in propane (Fig. 2) is split into two peaks in cyclopropane, at 5.5 and 7.9 eV.

Figures 7 and 8 show the dependence of the vibrationally inelastic DCSs on the incident electron energy. These spectra are dramatically different from those of propane (in Figs. 2 and 3) in that at least two narrower resonances can be discerned at about 2.6 and at 5.5 eV, apart from the very broad band peaking between 8 and 10 eV.

The resonance at 5.5 eV has truly remarkable properties. It is, to the best of our knowledge, the narrowest resonance reported for an alkane. This points to a high centrifugal bar-

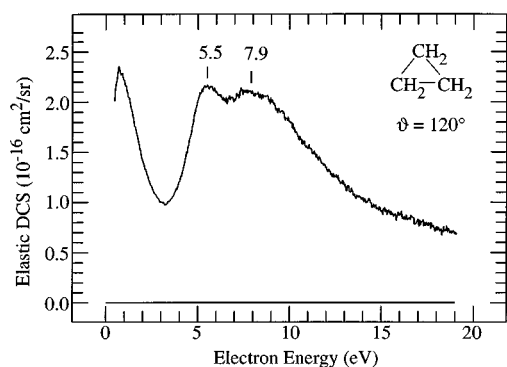


FIG. 6. Absolute elastic DCS in cyclopropane.

rier, that is a partial wave with high l , with no contribution of low l values. Remarkable is further the very high degree of selectivity in the vibrational excitation caused by the 5.5 eV resonance—it is dominant in the ν_3 ring stretch excitation and its two overtones (Fig. 7), and it is not discernible at all in the C–H stretch excitation and the CH_2 scissoring excitation (Figs. 7 and 8). It appears only very weakly in the $\nu_1 + \nu_2$ combination vibration and the ν_{11} ring deformation DCSs. This high degree of selectivity indicates a temporary occupation of an orbital localized on the carbon ring, with no coefficients on the hydrogen atoms.

We use the Koopmans' theorem¹⁹ (applicable to anions only with an empirical linear scaling relation²⁰ $\text{AE} = (\epsilon - 2.33)/1.31$ relating HF 6-31 G* virtual orbital energies ϵ , obtained from the Gaussian²¹ program, to an estimated attachment energy AE, both in eV) in an initial attempt to assign this resonance.^{7–9} We feel that this attempt is justified by the success of this approach to rationalize experimental energies of shape resonances in a wide range of situations and for unrelated kinds of orbitals (propellane,³ allene,²²

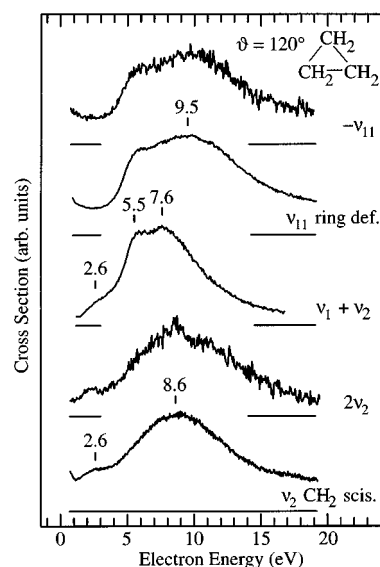


FIG. 8. Vibrationally inelastic cross sections for cyclopropane, continued from Fig. 7.

ozone²³), despite possible objections to the use of this crude approach for very short-lived resonances. Figure 9 summarizes the calculated results of Ref. 9 for propane and cyclopropane. As already pointed out in the preliminary reports,^{7–9} a shape resonance corresponding to a temporary occupation of the $1a'_2$ orbital explains very well the observed energy and vibrational excitation selectivity of the 5.5 eV resonance. The calculated energy is 5.1 eV, a very satisfactory agreement in view of the crude theoretical treatment. The $1a'_2$ orbital has nodes across the C–C bonds, which will be appreciably lengthened by a temporary capture of an elec-

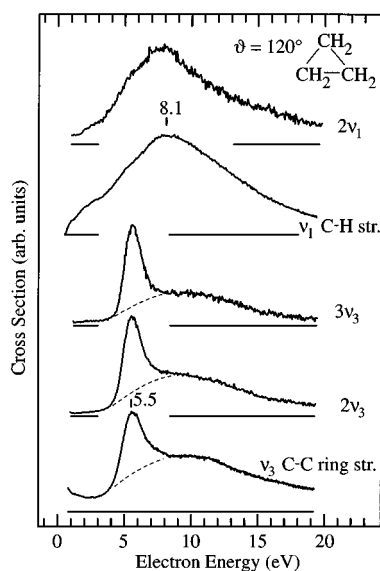


FIG. 7. Relative vibrationally inelastic cross sections for cyclopropane, recorded as a function of the incident electron energy.

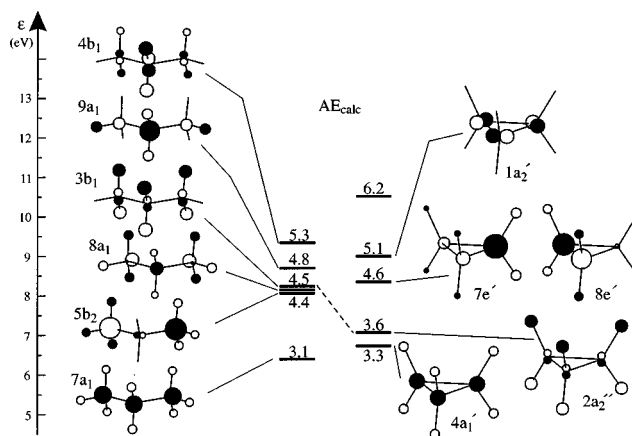


FIG. 9. Energies of HF/6-31G* virtual orbitals (scale on the left) and vertical attachment energies for propane and cyclopropane, estimated from the orbital energies using Koopmans' theorem and an empirical scaling relation as explained in the text. Schematic diagrams of the orbitals were drawn with MOPLOT (Ref. 28).

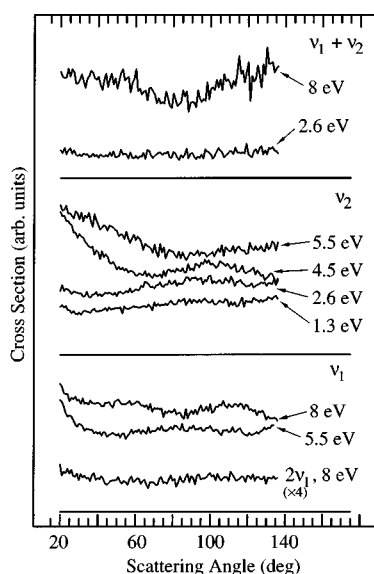


FIG. 10. Relative DCSs in cyclopropane recorded in function of the scattering angle.

tron, and has no coefficients on the H atoms, predicting that the C–H bond lengths will not be significantly changed.

A stringent test of this assumption is provided by the angular distributions, shown for selected vibrational peaks and electron energies in Figs. 10 and 11. Most of the curves resemble qualitatively the propane results (Fig. 4), being nearly isotropic. The variations with angle are not pronounced, and it is not possible to rationalize them in terms of a single partial wave. This result indicates the action of several overlapping resonances or resonances where two or more partial waves contribute significantly. An exception is the ring stretch excitation (ν_3 and its overtones) via the 5.5 eV resonance, with pronounced angular behavior.

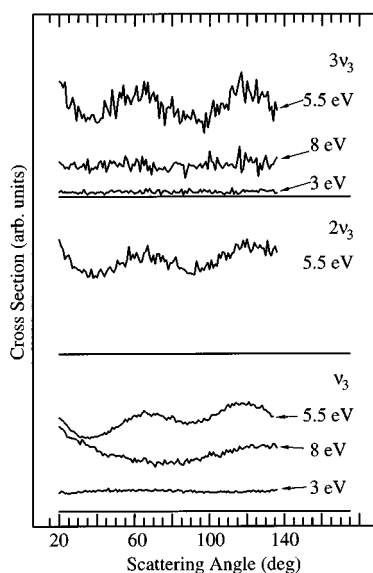


FIG. 11. Relative DCSs in cyclopropane recorded in function of the scattering angle, continued from Fig. 10.

We analyzed this angular distributions using the angular correlation theory developed by Read²⁴ and Andrick and Read.²⁵ This theory had been developed under the assumption that the angular distribution of the scattered electrons depends only on the symmetries of the states involved in the resonant process, it can be used for all types of molecules belonging to all symmetry groups, and allows the treatment of vibronic (vibrational and electronic) states, essential when dealing with polyatomic molecules. Since the angular momentum in the theoretical treatment appears as a parameter, the comparison of the measured and calculated angular behaviors of resonantly scattered electrons can give clear information about the symmetry of the resonant state in the case when only the first partial wave with the lowest angular momentum participates, or at least is strongly dominant in the formation and decay of the resonance. The cyclopropane molecule belongs to the D_{3h} symmetry group and the resonance at 5.5 eV is observed to lead to dominant excitation of the totally symmetrical (a_1') C–C ring breathing mode. Only one symmetry of the resonant state, namely a_2'' , resulted in a satisfactory agreement of experiment and theory. The first allowed partial wave in the entrance and exit channels is then $l=3$, $m=3$. In this particular case the expected angular dependence is:

$$\text{DCS} \propto 1 + \frac{1161}{97} \cos^2 \vartheta - \frac{3093}{97} \cos^4 \vartheta + \frac{2315}{97} \cos^6 \vartheta. \quad (1)$$

This calculated curve is symmetrical about 90° , with a minimum at 90° and a weak maxima at 60° and 120° , in agreement with the behavior of the ν_3 , $2\nu_3$, and $3\nu_3$ energy loss peaks in Fig. 11.

In an attempt to compare the theoretical and experimental angular dependencies more precisely, we note (see Fig. 7) that not only the “5.5 eV resonance,” but also the low energy wing of the extremely broad “10 eV resonance” contribute to the excitation ν_3 and its overtones at 5.5 eV. Angular distribution for $3\nu_3$ excitation just below and just above the “5.5 eV resonance” are nearly isotropic (top of Fig. 11). An approximation of the signal due to the “5.5 eV resonance” alone was consequently obtained by subtracting an isotropic background (corresponding to 25% and 18% of the total signal at 120° for $2\nu_3$ and $3\nu_3$, respectively) from the raw data in Fig. 11 to obtain the data shown as dots in Fig. 12.

The very satisfactory agreement of experiment and theory in Fig. 12 identifies the “5.5 eV resonance” unambiguously as a_2'' . It is worth emphasizing that although the original proposition of this assignment came from the application of the Koopmans’ theorem, the assignment is now based on angular distribution of the scattered electrons and does not depend on the validity of the Koopmans’ theorem!

There is a less dominant, but clear indication of another resonance peak at around 2.6 eV in Figs. 7 and 8. It appears as a shoulder in the DCS for CH_2 scissoring, its overtone, and combination with C–H stretch. It can also be discerned as a weak shoulder in the C–H stretch excitation DCS. There is no indication of this resonance in the ring stretch excita-

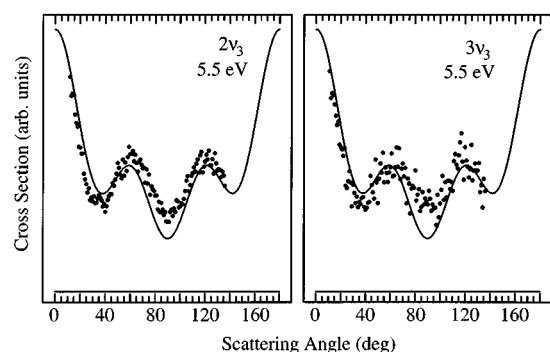


FIG. 12. Comparison of the shapes of the experimental angular distribution (dots) and the theoretical distribution given by Eq. (1) (line), for the excitation of ν_3 overtones by the a_2'' resonance at 5.5 eV. A constant (isotropic) background (amounting to 25% of the signal intensity at 120° for $2\nu_3$ and 18% for $3\nu_3$) was subtracted from the experimental spectra, as explained in the text.

tion. This selectivity indicates temporary occupation of an orbital with nodes between the H atoms on the same carbon, but not affecting the C–C bond. Inspection of the nodal properties of the virtual orbitals in Fig. 9 reveals the $2a_2''$ MO as a possible candidate for this resonance, since it has a node between the H atoms on each C atom, its temporary occupation should lead to an increase of the H–C–H angle. It is nominally weakly bonding along the C–C bonds, but this effect is likely to be compensated by the general “inflation” of the molecule following the increase of repulsive interactions in the presence of an extra electron. This assignment is less certain than the assignment of the “5 eV resonance,” however. Our attempts to describe the observed angular distribution in terms of a single partial wave failed for the 2.6 eV resonance, indicating that several partial waves contribute.

Virtual orbitals of propane are also included in Fig. 9 to illustrate the situation encountered when trying to apply the Koopmans’ theorem to linear alkanes. Six relatively closely spaced virtual orbitals are obtained, which are not very useful for the assignment of the very broad observed peak. The situation could be somewhat clarified by applying a form of the stabilization method, i.e., testing the sensitivity of the virtual orbital energies on the size of the basis set, in an attempt to identify some of the virtual orbitals as “discretized continuum states.” We do not apply this method here in the belief that a more elaborate scattering calculation is required in the propane case. Noteworthy in Fig. 9 is perhaps that the $3b_1$ orbital of propane is a “ π ” orbital closely related to the $2a_2''$ orbital of cyclopropane, and a possible candidate for the explanation of the enhanced excitation of the CH_2 deformation vibration at 3 eV (Fig. 1).

The excitation function for the superelastic peak $-\nu_{11}$ (electron-energy gain of 107 meV, see also Fig. 5) is also given in Fig. 8. As expected, its shape is identical to that of the inelastic ν_{11} peak.

The energy-loss spectra of ethylene oxide in Fig. 13 resemble closely the cyclopropane spectra in Fig. 5, bearing out the similarity of vibrational structure and of the scatter-

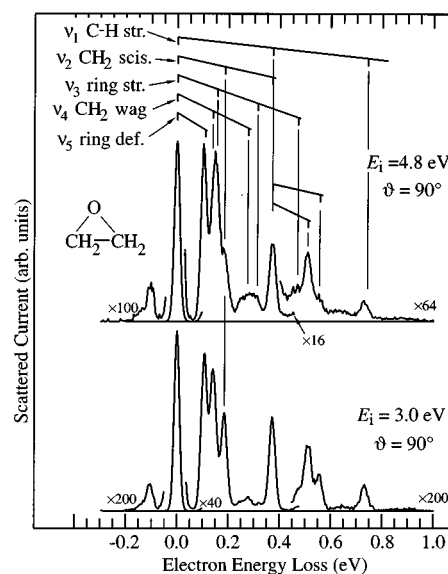


FIG. 13. Energy loss spectra of ethylene oxide.

ing mechanism in the two compounds. In particular note that the CH_2 scissoring vibration is relatively more intense in the 3 eV spectrum than it is in the 4.8 eV spectrum, indicating a resonant excitation analogous to the “2.6 eV resonance” of cyclopropane.

The vibrationally inelastic DCSs, shown as a function of the incident electron energy in Fig. 14, are also reminiscent of those in cyclopropane. The “5.5 eV resonance” of cyclopropane is lowered to 4.8 eV in ethylene oxide. Like the 5.5 eV resonance of cyclopropane, the 4.8 eV resonance of ethylene oxide is most pronounced in the C–C stretch excitation. The degree of selectivity of excitation which it causes is more difficult to judge than it is in cyclopropane, however,

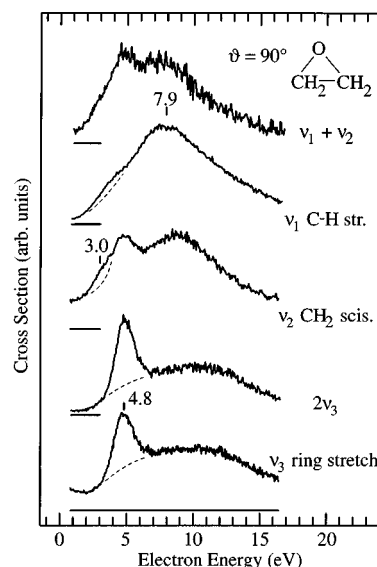


FIG. 14. Relative DCSs in ethylene oxide recorded in function of the incident electron energy.

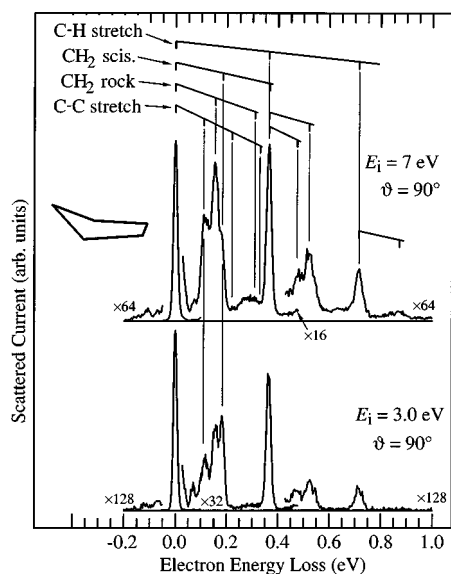


FIG. 15. Energy loss spectra of cyclopentane.

because the C–C stretch and the CH₂ scissoring vibrations are less well separated in ethylene oxide than they are in cyclopropane, and an overlap of the energy-loss bands (Fig. 13) may affect the spectra in Fig. 14. The weak appearance of the 4.8 eV resonance in the CH₂ scissoring may be due to this overlap, rather than to weaker selectivity. A broad weak shoulder may just be discerned at around 3 eV in the CH₂ scissoring and the C–H stretch excitation curves in Fig. 14, indicating a resonance analogous to the 2.6 eV resonance in cyclopropane. Its visibility is less clear than in cyclopropane because the 4.8 eV resonance and the shoulder at 3 eV are less separated than the corresponding features in cyclopropane and consequently overlap more.

Cyclopentane has a large number of vibrational modes,²⁶ but related types are again grouped around certain frequencies, permitting the (somewhat tentative) assignment of the peaks observed in the energy-loss spectra to certain types of vibrations, indicated in Fig. 15. The spectra resemble qualitatively those of the previous compounds: A prominent group of three peaks (probably comprising more than three vibrations) is found in the 0.10–0.20 eV energy-loss range, comprising the C–C stretch, the CH₂ rocking, and the CH₂ scissoring vibrations. Note that, as in the previous compounds, the CH₂ scissoring mode is more prominent at 3 than at 7 eV. A weaker group of unresolved signal is found in the 0.2–0.35 eV range, comprising the overtones and combinations of the vibrations in the 0.1–0.2 eV range. Finally, a prominent C–H stretch band follows, peaking at 365 meV (it is wider than the elastic peak and thus consists of several vibrations). Overtones of the C–H group and combinations of C–H with the vibrations in the 0.1–0.2 eV range can be discerned at higher energy losses. Low frequency vibrations, at around 40 and 70 meV, are also excited.

The excitation functions in Fig. 16 also bear some reminiscence of the results in cyclopropane, but less than the ethylene oxide results. A relatively narrow band is found at

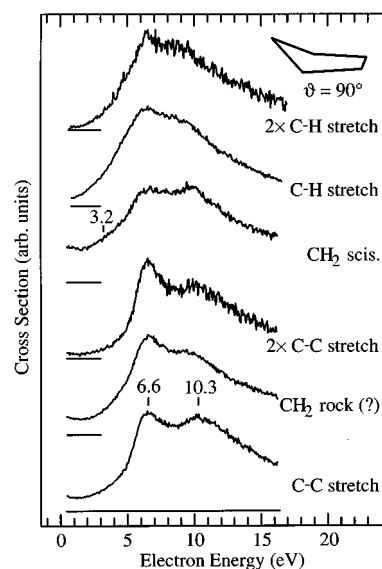


FIG. 16. Relative DCSs in cyclopentane recorded in function of the incident electron energy.

6.6 eV, possibly related to the 5.5 eV resonance of cyclopropane. The selectivity is similar but less strict than in cyclopropane—the 6.6 eV band is more prominent in the C–C stretch excitation functions, but can be discerned to some degree even in the remaining excitation functions in Fig. 16. The reduced selectivity may be interpreted as a consequence of the smaller symmetry of cyclopentane:²⁷ In contrast to cyclopropane there are no orbitals located exclusively on the carbon ring, having zero coefficients on the hydrogen atoms.

The onset of the resonant signal in the upper three curves in Fig. 16 is at somewhat lower energy than in the lower three curves, indicating a resonant process in the 2–4 eV region, exciting preferentially the CH₂ scissoring and the C–H stretch vibrations. This finding resembles that in cyclopropane, although it is less pronounced.

The energy-loss spectra of cyclohexane, Fig. 17, are also reminiscent of those of the previous compounds, with a prominent band in the 0.1–0.2 eV range, which can be rationalized well as excitation of the totally symmetrical vibrations ν_3 (CH₂ scissoring), ν_4 (CH₂ rocking), and ν_5 (C–C stretch), a prominent C–H stretch band, and the overtone and combination bands (vibrational frequencies are taken from Ref. 15). Excitation of low frequency vibrations may be discerned below 0.08 eV, as in both previous “floppy” compounds, propane, and cyclopentane.

The features in the excitation curves of cyclohexane, Fig. 18, are even broader than in cyclopentane and the resemblance with cyclopropane is even weaker. There is a band at 7.5 eV, which resembles somewhat the 5.5 eV cyclopropane band in terms of energy, but not in terms of selectivity, it is not prominent in the C–C stretch excitation. A shoulder at around 4.2 eV resembles somewhat the cyclopropane 2.6 eV resonance, also in that it can be discerned in the

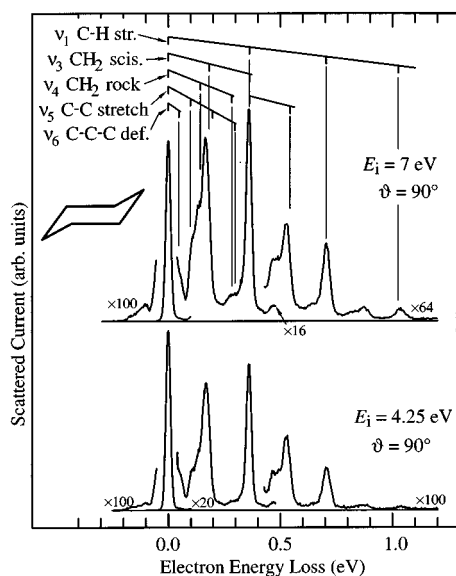


FIG. 17. Energy loss spectra of cyclohexane.

CH_2 scissoring and the C–H modes, but not in the C–C stretch mode.

HF virtual orbitals and Koopmans' theorem are not very helpful in assigning the resonances in cyclopentane and cyclohexane because too many orbitals result from the calculations. They have many nodes and do not permit qualitative predictions of selectivity of vibrational excitation, in agreement with the experimental observations in Figs. 16 and 18, where only weak selectivity is found.

IV. CONCLUSIONS

Vibrational excitation functions in linear alkanes such as ethane (Ref. 4) or propane (this work) exhibit only one ex-

tremely broad band, with a gradual onset around 3 eV, peaking in the 7–8 eV range, and extending to more than 15 eV. The energy and width of this band depend only little on which compound and which vibration is considered. This result resembles the observation in H_2 , where a single extremely short-lived and consequently broad σ^* resonance causes a band in the vibrational excitation function. These observations may give rise to the impression that a single, uniform scattering process is responsible for the vibrational excitation in linear alkanes, with a “vertical” attachment energy of about 8 eV, far above the attachment energies of alkenes, such as ethene (vertical attachment energy 1.8 eV²).

Profound changes are encountered in the attachment spectra, however, when going from the linear alkanes to otherwise closely related cyclic compounds: several distinguishable resonances emerge from the extremely broad band in the linear alkanes, the lowest being at much lower energies than the 8 eV peak of the linear alkanes. The second of these resonances (at 5.5 eV) can be assigned unambiguously in cyclopropane. For cyclopropane and ethylene oxide, the energies of these narrower resonances, and the selectivity of vibrational excitation which they cause can be rationalized well in the perceptually useful terms of a temporary capture of the incident electron in distinct virtual orbitals, just as is customary for the π^* resonances of unsaturated compounds.

In view of this it is interesting that, despite the obvious dramatic differences, parallels are found in the vibrational excitation patterns of *n*-propane and of the cyclic compounds, in particular the more prominent excitation of the CH_2 scissoring vibration at lower energies, 2–4 eV. This indicates, that even the extremely broad band in alkanes may be usefully viewed as several overlapping resonances, not discernible individually in the spectra because of the overlap. These resonances become distinguishable in the cyclic compounds primarily not because of large shifts in energy, but because the higher symmetry and the rigidity of the molecules cause partial waves with higher *l* to dominate the scattering, resulting in higher centrifugal barriers, longer resonance lifetimes and narrower widths. This view has a consequence relevant to chemistry, namely that the notion of alkanes having a vertical electron attachment energy of 8 eV (i.e., vert. electron affinity of –8 eV) is not appropriate, it appears much more appropriate to consider the lowest attachment energy of even linear alkanes to be around 3 eV, where pronounced resonant vibrational excitation sets in (although the term “vertical” is not applicable because no distinct band is observed). This is still well above, but much closer to, the vertical attachment energies of small unsaturated hydrocarbons like ethene (attachment energy of 1.8 eV²).

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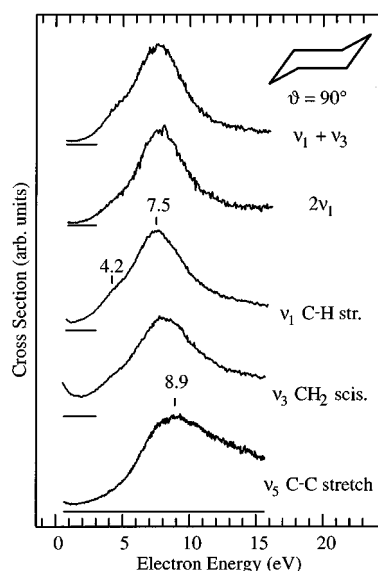


FIG. 18. Relative DCSs in cyclohexane recorded in function of the incident electron energy.

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