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Vibrational Excitation by Electron Impact in Cyclopropane. Electron Affinity and σ^* Orbitals

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This communication reports the vertical gas-phase electron affinity (EA) of cyclopropane to be −2.6 ± 0.3 eV, much larger than reported so far and comparable with that of unsaturated compounds, such as tetramethylethylene (−2.27 eV[1]). The cyclopropane radical anion is thus more stable than previously assumed.

The finding has a general bearing on properties of σ^* orbitals in hydrocarbons, which play, together with the occupied σ orbitals, an important role in "through-bond" coupling of chromophores and thus affect electron- and excitation-transfer through saturated bridges.[2] Information on virtual orbitals is generally obtained by using electron transmission spectroscopy[3] (ETS) to detect short-lived negative ions (resonances) and relating them to the virtual orbitals by means of Koopmans' theorem.[4] Direct information on the hydrocarbon σ^* orbitals is sparse because they rarely cause pronounced bands in ETS.[5] The only exceptions are cyclopropane[6] and a few other saturated cyclic hydrocarbons,[5,7] where ETS revealed relatively narrow σ^* bands in the 4–6-eV range.

This communication reports the study of cyclopropane by the more powerful though instrumentally more demanding alternative to ETS, the measurement of resonant vibrational excitation by electron impact.[8] This method has already been applied to hydrocarbons, for example methane,[9] ethane,[10] and ethene,[11] and has revealed very broad bands with maxima in the 6–8-eV range, sometimes assigned to σ^* resonances but generally considered too diffuse to justify the application of Koopmans' theorem.

Figure 1 shows a sample energy loss spectrum[12] of cyclopropane, recorded at the energy of the 5.5-eV resonance already known from ETS.[6] Not all of the 14 vibrations[13] are strongly excited, in line with the generally observed selectivity of resonant excitation, that is, excitation induced by geometry changes in the short-lived anion resulting from temporary capture of the incident free electron in a virtual orbital.[14] Most of the vibrations in Figure 1 can be assigned as totally symmetric C–H stretch ν_1, CH_2 scissoring ν_2, and ring stretch ν_3.[15]

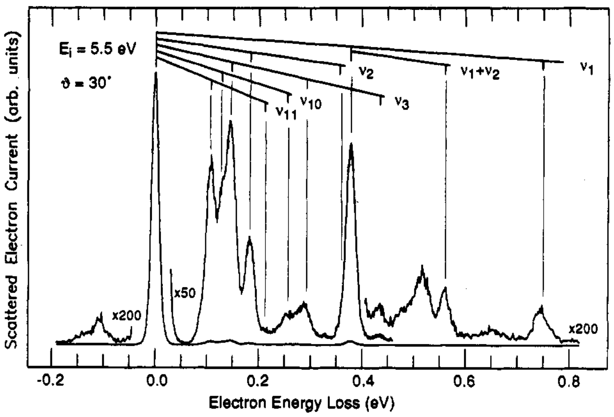

Figure 1. Vibrational electron energy loss spectrum of cyclopropane. The vertical lines indicate standard vibrational energies[13] (lines pointing to overtones include small anharmonicities).

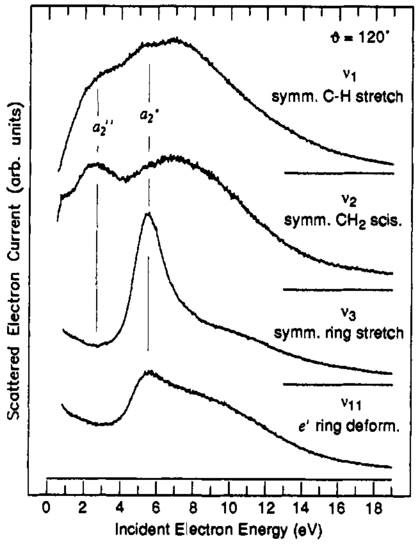

Figure 2. Excitation functions of four selected vibrational features. Proposed assignments of two features to a_2'' and a_2' resonances are indicated.

Bands in the curves showing the dependence of the excitation of these vibrations on incident electron energy (Figure 2) are

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[10] Tanaka, H.; Boesten, L.; Matsunaga, D.; Kudo, T. *J. Phys. B: At. Mol. Phys.* **1988**, *21*, 1255.

[11] Walker, I. C.; Stamatovic, A.; Wong, S. F. *J. Chem. Phys.* **1978**, *69*, 5532.

[12] The spectrometer has been described previously.[5] Spectra in Figure 1 were recorded with 15 meV and those in Figure 2 with 25 meV resolution. They are not corrected for the variations of instrument's sensitivity, which is, above 1 eV, a monotonously decreasing function of electron energy. The measured band position is the attachment energy (AE). Electron affinity (EA) is defined as the AE multiplied by −1.

[13] Shimanouchi, T. *Tables of Molecular Vibrational Frequencies, Consolidated Volume I*; National Standard Reference Data Series 39; U.S. National Bureau of Standards; U.S. Government Printing Office: Washington, DC, 1972.

[14] Direct (not related to resonances) excitation of IR-active vibrations may also occur but are important only at low electron energies (<1 eV) and low scattering angles. This effect (in the present context undesirable) is diminished by recording the spectrum in Figure 1 at a relatively large incident energy and the spectra in Figure 2 at a large scattering angle. Remaining excitation of overlapping IR-active vibrations probably causes the background, monotonously decreasing with increasing energy in the 0–3-eV range in Figure 2. (This background is nearly absent in the excitation functions of overtones, not shown.)

[15] Which vibrations are actually excited cannot always be determined on the basis of the peak position alone. For example, ν_2 (183 meV) and ν_9 (178 meV) are not distinguishable with the present resolution, nor are ν_1 (377 meV), ν_6 (385 meV), ν_8 (375 meV), and ν_{12} (382 meV). Frequencies and labels of only the totally symmetric (a_1') vibrations were given in Figure 1 in these cases, this assignment being most probable since a_1' vibrations would be expected to be excited by the nondegenerate a_2' resonance at 5.5 eV. The remaining slight ambiguity in the assignment does not affect the conclusions drawn below from the selectivity of the excitation, because the vibrations with similar frequencies are of the same type, CH_2 scissoring in the case of ν_2 and ν_9, C-H stretch for ν_1, ν_6, ν_8, and ν_{12}. Two low-lying vibrational features cannot be assigned to totally symmetric vibrations, and a probable assignment to ν_{10} and ν_{11} (both e′) is indicated in Figure 1. They could be excited by Jahn–Teller distortion of resonances with occupation of the degenerate e′ and e″ orbitals, which could be manifested by the broad feature in the 4–12-eV range in the ν_{11} excitation function in Figure 2. The large width of the feature makes this assignment uncertain at this point however.

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indicative of formation of a temporary negative ion, that is, within the concept of Koopmans' theorem, of capture of the incident electron in a virtual orbital.

The most prominent feature in Figure 2 is the band at 5.5 eV, already known from ETS.[6] It is surprisingly narrow for a saturated hydrocarbon and for its relatively high energy. The fact that this band is prominent in the symmetrical ring stretch ν_3 (and its overtones) indicates that the orbital involved has nodes between the carbon atoms, its temporary occupation causing substantial prolongation of the C–C bonds. The near absence of this band in the C–H stretch and scissoring vibrations further indicates that the orbital is located primarily on the carbon ring and has very small (or 0) coefficients at the hydrogen atoms, thus not affecting the C–H bond length and the H–C–H angle. Angular distributions of electrons having excited ν_3 and its overtones at 5.5 eV indicate f-wave scattering and consequently an orbital with nodal structure resembling an atomic f-orbital. Only one of the virtual orbitals of cyclopropane, the a_2' orbital (Figure 3), satisfies these conditions. This assignment deviates from the original ETS interpretation but receives further qualitative support from scattering calculations.[16]

An unexpected feature is the band with a maximum at 2.6 ± 0.3 eV in the ν_2 excitation in Figure 2, indicating a vertical electron affinity of −2.6 ± 0.3 eV for cyclopropane. This band also appears as a shoulder in the excitation functions of the ν_1 and the $\nu_1 + \nu_2$ vibrations (the latter is not shown). This selectivity points to an orbital antibonding with respect to the C–H and H–H distances but nonbonding with respect to the C–C distance. The angular distribution does not show pronounced maxima, indicating a mixture of partial waves in this case. The a_2'' orbital shown in Figure 3 appears to best fit these observations, although the assignment is less unambiguous in this case. The even lower-lying (at the HF/6-31G level of theory) a_1' LUMO also represents a possible assignment, although the s-wave contribution to the scattering for an a_1' orbital is often assumed to imply an excessively short lifetime of the resonance, preventing its observation. The a_2'' assignment does, however, parallel the assignment of K-shell excited states.[17]

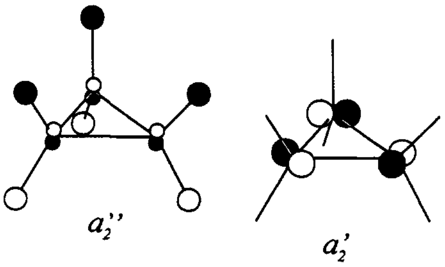

Figure 3. Schematic diagrams of the a_2'' and a_2' virtual orbitals (drawn with the program MOPLOT[18]).

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