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# Temporary negative ions and vibrational excitation in $CH_3Cl$ and $CD_3Cl$

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The excitation of vibrational modes of molecules by slow electrons is well-known to be greatly enhanced by the formation of temporary negative ion states.[1] The energies and symmetry assignments of these transient intermediates in $CH_3Cl$ have been the subject of recent controversy. A broad resonance at 3.45 eV was first observed by Burrow, Modelli, Chiu, and Jordan[2] using electron transmission spectroscopy (ETS) (Ref. 3) and assigned to the temporary occupation of the lowest C–Cl $\sigma^*$ orbital of $a_1$ symmetry $(8a_1)$. Benitez, Moore, and Tossell[4] also observed the same feature using ETS but stated that "there are no obvious resonances in the ET spectrum." Furthermore, from comparisons of data from ETS and inner-shell electron energy-loss spectra in the chloromethanes, they argued that the $a_1$(C–Cl) resonance in $CH_3Cl$ should lie near 1.3 eV, although no structure in the scattering cross section was observed near this energy.

Falcetta and Jordan[5] responded to Benitez *et al.*[4] with more sophisticated calculations than had been used by Burrow *et al.*[2] to support the original ETS measurements. Their results, which employed stabilization techniques, were in complete accord with the original assignments. Guerra, Jones, Distefano, Scagnolari, and Modelli[6] independently reached the same conclusion by means of multiple scattering $X\alpha$ calculations.

Most recently Wan, Moore, and Tossell[7] again reassigned the resonances in the chloromethanes on the basis of a comparison with attachment energies and term values derived from inner-shell electron energy-loss spectroscopy as well as calculated term values. In particular they argued that occupation of the $a_1$ orbital of $CH_3Cl$ yields a stable negative ion and that the 3.45 eV feature observed in electron scattering is due to a resonance of $e$ symmetry.

In this paper we describe the results of an electron scattering experiment designed to test directly the symmetry of the 3.45 eV resonance. The concepts are as follows. From symmetry considerations alone, temporary occupation of an orbital excites the nuclei in directions described by the symmetrized square of the irreducible representation of the state involved.[8,9] Occupation of an $a_1$ orbital will lead therefore to excitation of totally symmetric, $a_1$, vibrational modes. Occupation of an $e$ orbital, on the other hand, will excite both $a_1$ and $e$ modes. As discussed by Gallup,[9] another mechanism exists that leads to excitation of modes of the same symmetry as that of the resonance. In the case of $CH_3Cl$, this consideration does not lead to any additional modes.

Within the symmetry limitations, the actual strength of excitation of a given mode depends on the charge distribution in the particular molecular orbital. The $8a_1$ $\sigma^*$ orbital is strongly antibonding between the carbon and chlorine atom and will be designated $8a_1$(C–Cl). The $4e$ orbital as well as a higher-lying $a_1$ orbital are both primarily C–H antibonding.

Table I provides a listing of the fundamental vibrational modes of $CH_3Cl$ and $CD_3Cl$ with symmetries, energies and an indication of the type of deformation.[10] Combining both the symmetry and charge distribution considerations, we argue qualitatively that if the 3.45 eV feature corresponds to filling of the $8a_1$(C–Cl) orbital, we expect the strongest excitation to occur in the $v_3^{C-Cl}(a_1)$ mode at 90.9 meV, weaker excitation of the $v_2^{CH_3}(a_1)$ and $v_1^{CH}(a_1)$ modes and no excitation of $v_6(e)$, $v_5^{CH_3}(e)$, or $v_4^{CH}(e)$. On the other hand, if the resonance is of $e$ symmetry, we would anticipate only weak excitation of $v_3^{C-Cl}(a_1)$ because of the unfavorable charge distribution near the C–Cl bond, and strong excitation of certain of the $v_2^{CH_3}(a_1)$, $v_1^{CH}(a_1)$ and $v_6(e)$, $v_5^{CH_3}(e)$, and $v_4^{CH}(e)$ modes. A detailed examination of the shape of the $e$ orbital is required to see which particular modes would be most effectively driven.

The electron energy loss spectra shown in Fig. 1 were measured with a hemispherical electrostatic monochromator and analyzer similar to those described by Comer and Read[11] and Boness and Schulz.[12] A previous application to vibrational excitation in 1,4-cyclohexadiene is given elsewhere.[13] In the present study, the overall energy resolution (FWHM) is 25–30 meV. The loss spectra of Fig. 1 were acquired at a scattering angle of 100° and an incident electron energy of 3.5 eV. Lines indicating the energies of the vibrational modes are shown for each gas. We note here that all of the fundamental vibrational modes are dipole and Raman active.[10] The large scattering angle significantly reduces the contribution of these nonresonant processes to the spectra.

The $CH_3Cl$ spectrum (upper curve) displays the strongest excitation in the $v_3^{C-Cl}$ mode at 90.9 meV. At first glance, the two overtones of this mode $2v_3$ and $3v_3$, at 181.8 and 272.7 meV, respectively, also appear to be excited. Unfortunately $v_5^{CH_3}(e)$ at 180.7 meV lies unresolvably close to $2v_3$, preventing this simple assignment. Similarly $v_3^{C-Cl}(a_1) + v_5^{CH_3}(e)$ at 271.6 meV lies very near $3v_3$. Furthermore, the possibility that the modes of $e$ symmetry are making a contribution is reinforced by the appearance of the peak near 378 meV, which can be assigned with some certainty to $v_4(e)$.

To break the near degeneracy of the $2v_3$ and $v_5$ levels, energy loss data were also measured in $CD_3Cl$ (from MER Isotopes), shown in the lower curve of Fig. 1. In this mol-

TABLE I. The vibrational modes of $CH_3Cl$ and $CD_3Cl$, their symmetries, energies (meV), and the types of deformation.

| Mode (symmetry) | Deformation | $CH_3Cl$ energy (meV) | $CD_3Cl$ energy (meV) |
|---|---|---|---|
| $\nu_3^{C-Cl}$ ($a_1$) | C–Cl stretch | 90.9 | 86.3 |
| $\nu_6$ ($e$) | $H_3 \equiv$ C–Cl bend | 126.1 | 96.3 |
| $\nu_2^{CH_3}$ ($a_1$) | $CH_3$ | 168.3 | 127.8 |
| $\nu_5^{CH_3}$ ($e$) | $CH_3$ | 180.7 | 131.4 |
| $2\nu_3$ | | 181.8 | 172.6 |
| $3\nu_3$ | | 272.7 | 259.0 |
| $\nu_1^{CH}$ ($a_1$) | CH stretch | 368.4 | 268.4 |
| $\nu_4^{CH}$ ($e$) | CH stretch | 377.8 | 283.9 |

ecule, the overtone $2\nu_3$ at 172.6 meV is clearly identifiable and has a magnitude of approximately one-fifth that of the fundamental. The presence of such a harmonic demonstrates immediately that the C–Cl stretch motion is strongly excited by the 3.5 eV resonance. The $CD_3Cl$ data also indicate that in $CH_3Cl$ the second loss peak contains a considerable contribution from $\nu_5(e)$, as does the peak near $3\nu_3$ from $\nu_3 + \nu_5$.

The results thus far seem to argue for assigning the 3.5 eV resonance to both the $a_1$ and $e$ orbitals. This conflict is resolved by looking at the excitation probabilities of the



FIG. 2. Relative excitation functions for the indicated vibrational modes of $CH_3Cl$ as a function of electron energy. The scattering angle is 100°.

modes as a function of electron energy. Figure 2 shows the excitation functions of the indicated modes measured at a scattering angle of 100°. Excitation of the $\nu_3$ mode in $CH_3Cl$ (top curve) is characterized by a peak near 3 eV with a full width at half-maximum of $\approx 2.5$ eV similar to that observed in the ET spectrum.[1] In contrast, the excitation function for $\nu_4^{CH}(e)$, middle curve, peaks substantially higher, near 5 eV, and is roughly twice as broad. These quite different characteristics argue for a second resonance in this region capable of exciting $e$ vibrational modes, and symmetry considerations lead to the $4e$ resonance. This interpretation explains quite readily the presence of $e$ vibrational modes in the energy loss spectra of Fig. 1; the upper resonance is broad enough to overlap considerably the lower resonance at an impact energy of 3.5 eV.

The bottom curve of Fig. 2 shows the excitation function for the composite peak $2\nu_3$ and $\nu_5$. It exhibits a maximum at 3.2 eV arising from the $2\nu_3$ contribution but falls off somewhat slower at high energy than that for $\nu_3$ due to the additional excitation of $\nu_5$, which is expected to resemble the function for $\nu_4$.

Preliminary measurements of the angular distribution of electrons exciting the $\nu_3$ mode at 3.5 eV show a relatively flat distribution above an angle of 30°, which is also consistent with an $a_1$ resonance. In conclusion, electron energy loss data show clearly that the 3.5 eV feature in the
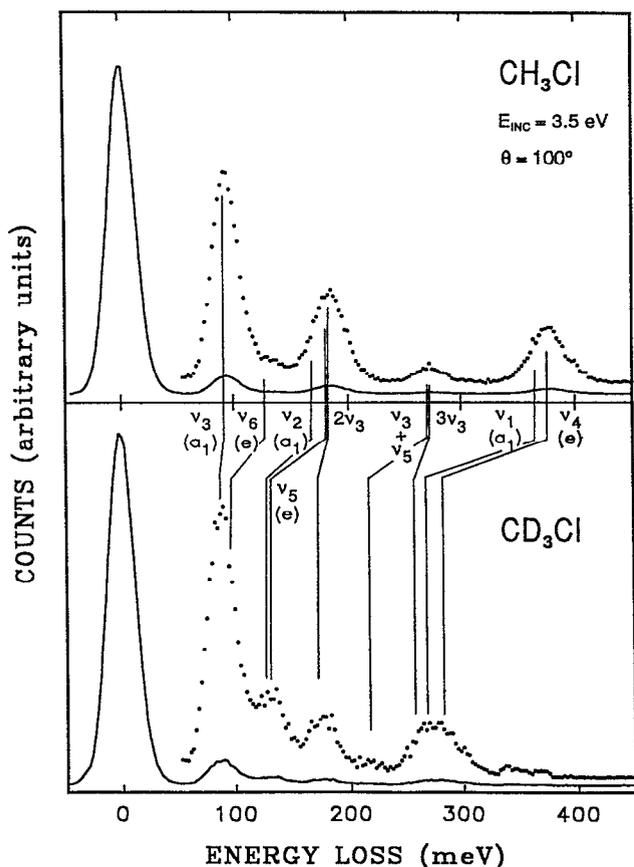


FIG. 1. Electron energy loss spectra in $CH_3Cl$ (upper curve) and $CD_3Cl$ (lower curve). The incident electron energy is 3.5 eV and the scattering angle is 100°. The vertical lines correlate the loss peaks in the two gases and are labeled with the vibrational modes.
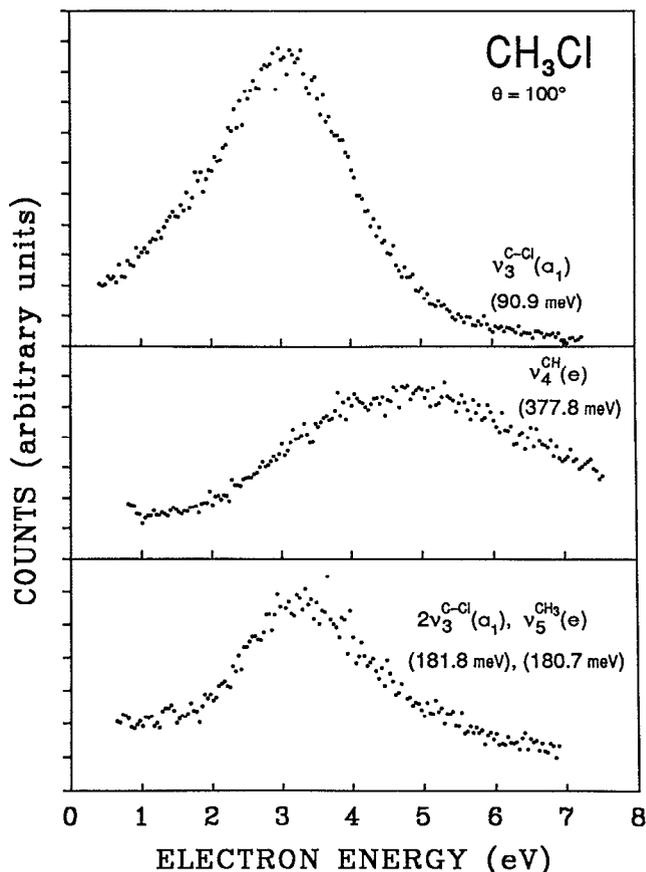
electron scattering from $CH_3Cl$ is caused by the temporary occupation of the $8a_1$ (C–Cl) molecular orbital rather than the $4e$ orbital assigned by Wan et al.[7] Evidence is also presented to show that the resonance due to occupation of the $4e$ orbital lies near 5 eV and is much greater in breadth, partially overlapping the $a_1$ resonance. The relative excitation functions of Fig. 2 are not completely free of slow variations in the electron-optical instrument function over the range of energies shown. Absolute differential cross section measurements in progress will provide more accurate determinations of the cross section shapes and peak energies.

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