SUPPLEMENTARY INFORMATION for

Dissociative electron attachment to carbon tetrachloride probed by velocity map imaging

Anirban Paul,1 Dhananjay Nandi,1,* Daniel S. Slaughter,2 Juraj Fedor,3 and Pamir Nag3,†

1Indian Institute of Science Education and Research Kolkata, Mohanpur 741246, India
2Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
3J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences,
Dolejškova 2155/3, 182 23 Prague, Czech Republic

I. THRESHOLD ESTIMATION OF THE THREE-BODY AND MANY-BODY DISSOCIATION CHANNELS

A. Cl⁻ dissociation channels

The threshold of channel (c) in Table I of the main text can be estimated using the formula:

\[ E_{Th} = D(\text{CCl}_3 - \text{Cl}) + D(\text{CCl}_2 - \text{Cl}) - \text{EA}(\text{Cl}) \]
\[ = (3.0 + 3.7 - 3.61) = 3.09 \text{ eV} \]

Where, D(\text{CCl}_3-\text{Cl}), D(\text{CCl}_2-\text{Cl}), and D(\text{CCl}-\text{Cl}) are bond dissociation energies (BDEs) of \text{CCl}_3-\text{Cl}, \text{CCl}_2-\text{Cl}, and \text{CCl}-\text{Cl} respectively.

On the other hand, the threshold of channel (d) in Table I of the main text can be estimated using the formula:

\[ E_{Th} = D(\text{CCl}_3 - \text{Cl}) + D(\text{CCl}_2 - \text{Cl}) + D(\text{CCI} - \text{Cl}) \]
\[ - D(\text{Cl} - \text{Cl}) - \text{EA}(\text{Cl}) \]
\[ = (3.0 + 3.7 + 3.4 - 2.4 - 3.61) = 4.09 \text{ eV} \]

Similarly, that for channel (e) in Table I of the main text becomes:

\[ E_{Th} = D(\text{CCl}_3 - \text{Cl}) + D(\text{CCl}_2 - \text{Cl}) + D(\text{CCl} - \text{Cl}) \]
\[ - \text{EA}(\text{Cl}) \]
\[ = (3.0 + 3.7 + 3.4 - 3.61) = 6.49 \text{ eV} \]

B. Cl₂⁻ dissociation channels

The threshold energy for channel (a) in Table IV of the main text for the production of Cl₂ can be estimated using the formula:

\[ E_{Th} = D(\text{CCl}_3 - \text{Cl}) + D(\text{CCl}_2 - \text{Cl}) - \text{EA}(\text{Cl}_2) \]
\[ - D(\text{Cl} - \text{Cl}) \]
\[ = (3.0 + 3.7 - 2.4 - 2.9) = 1.4 \text{ eV} \]

On the other hand, an additional C–Cl bond break is required for the channel (c) in Table IV. The threshold energy therefore can be estimated using the formula:

\[ E_{Th} = D(\text{CCl}_3 - \text{Cl}) + D(\text{CCl}_2 - \text{Cl}) - \text{EA}(\text{Cl}) \]
\[ - D(\text{Cl} - \text{Cl}) \]
\[ = (3.0 + 3.7 - 2.4 - 2.9 + 3.4) = 4.8 \text{ eV} \]

C. CCl₂⁻ dissociation channels

The threshold energy in Table V of the main text for channel (a) for the production of CCl₂ can be estimated using the formula:

\[ E_{Th} = D(\text{CCl}_3 - \text{Cl}) + D(\text{CCl}_2 - \text{Cl}) - \text{EA}(\text{CCl}_2) \]
\[ = (3.0 + 3.7 - 1.8) = 4.9 \text{ eV} \]

On the other hand, that for channel (b) can be estimated using the formula:

\[ E_{Th} = D(\text{CCl}_3 - \text{Cl}) + D(\text{CCl}_2 - \text{Cl}) - D(\text{Cl} - \text{Cl}) \]
\[ - \text{EA}(\text{CCl}_2) \]
\[ = (3.0 + 3.7 - 2.4 - 1.8) = 2.5 \text{ eV} \]

II. ANALYSIS OF ANGULAR DISTRIBUTIONS OF Cl₂⁻ AND CCl₂⁻ IONS

The expression for the angular distribution of the fragment negative ions from the DEA to the diatomic molecule was first given by O’Malley and Taylor [1]. The expression is as follows:

\[ I(\theta, \phi, k) = \sum_{\mu} \sum_{l=\mu} a_{\mu}(k) Y^\mu_l(\theta, \phi) e^{il\Lambda} |^2 \]  \hspace{1cm} (1)

where \( a_{\mu}(k) \) are energy-dependent expansion coefficients, \( k \) is the incident electron momentum, \( Y^\mu_l(\theta, \phi) \) are the spherical harmonics, \( \mu \) is the difference in the projection of the angular momentum along the inter-nuclear axis for the neutral molecular state and the negative ion resonance state, given as \( \mu = |\Lambda_f - \Lambda_i| \), \( l \) is the angular momentum of the incoming electron with values given by \( l \geq |\mu| \) and \( (\theta, \phi) \) are the polar angles of the negative ion fragments with respect to the incident electron direction.

* also at Center for Atomic, Molecular and Optical Sciences & Technologies, Joint initiative of IIT Tirupati & IISER Tirupati, Yerpedu, 517619, Andhra Pradesh, India
† pamir.nag@jh-inst.cas.cz
Later Azaria et al. [2] extrapolated the expression for polyatomic molecules and found the angular distribution of the negative ion fragments averaging over $\phi$. The expression is as follows:

$$ I(\theta) = \frac{1}{2\pi} \int_0^{2\pi} \left| \sum_{i\mu \epsilon \lambda} i^l e^{i\lambda l} a_{l\mu} X_{l\mu}^l(\theta, \phi) \right|^2 d\phi $$

where $X_{l\mu}$ are the basis functions for the irreducible rep-
The basis functions for different states with different symmetries for molecules with Td point group symmetry are listed in Table I. There are five irreducible representations A1, A2, E, T1, and T2 under the Td point group symmetry. Different electronic states, therefore, can be represented as these irreducible representations. The A1 and A2 are two non-degenerate irreducible representations, while E is the doubly degenerate one. On the other hand, T1 and T2 are two triply degenerate representations. The basis functions representing the molecular orbitals are defined with respect to this axis.

The experimentally obtained angular distributions of Cl2− and CCl2− ions for 6.0 eV incident electron energy are shown in Figs. 1 (a)-(d) and Figs. 2 (a)-(d) respectively, along with the fits for different resonant symmetries considering direct bond breaking.

As discussed in the main text, theoretical calculation by Tossell and Davenport [4] and, later by Curik et al. [5] found a broad resonance at about 9 eV having E-symmetry. On the other hand, the Schwinger multichannel calculations with the static-exchange approximation by Moreira et al. found this feature at about 8 eV.[6]

The character table shows that l = 2 and 4 partial waves are allowed (up to g-wave) for E resonant symmetry. As a result, there should be forward-backward asymmetry in the angular distribution of the fragment anions. On the other hand, the experimentally obtained angular distribution exhibits a good amount of forward-backward asymmetry.

The blue solid curve in Fig. 1 (c) and 2 (c) represents the best fit with E resonant symmetry under the Td point group symmetry considering the axial recoil approximation for Cl2− and CCl2− ions respectively. Under this approximation, the ejection directions of both the Cl2− and CCl2− ions are perpendicularly outward [Figs. 11 and 14 in the main text] through the center of each face of the cube [Making half bond angle = 109°/2 = 54.75° with the C−Cl bond]. For the fitting, we have considered only the d-partial wave (l = 2). This suggests that most of the Cl2− ions should be ejected perpendicular to the electron beam direction and can not explain the observed angular distribution or forward-backward asymmetry. This is also true for the CCl2− ions.

The Vacuum Ultraviolet (VUV) absorption spectra of CCl4 on the other hand, suggests the presence of n → σ∗ (2t1 → 7a1) band at around 6.5 eV.[7, 8] Therefore, this 6 eV resonance might be a core excited Feshbach resonance. Therefore, the electronic configuration of the resonance will be (core) 2t1 7a1 with T1 symmetry. In Figs. 1 (b) and 2 (b), we have shown the fit to the angular distribution of Cl2− and CCl2− ions respectively with T1 resonant symmetry considering the simple direct bond breaking approximation.
the $f$ and $g$ partial waves produces this asymmetry. However, the fit for the direct bond-breaking model cannot explain the distribution completely. Also, the effect of the rotation of the CCl$_4$ TNI before getting dissociated cannot be ignored. However, the rotation effect does not have a bias in the forward or backward direction of the electron beam. Therefore, we have also fit the distributions considering the rotation of the CCl$_4$ TNI.

From Figs. 1 (a)-(d), it can be seen that the best fit to the angular distribution of Cl$^-$ ions is for $A_1$ resonant symmetry under axial recoil approximation. This is also the case for CCl$_4^-$ ions [Figs. 2 (a)-(d)].

Although it cannot completely justify the experimentally observed angular distribution, this symmetry can explain the observed forward-backward asymmetry. The discrepancy between the observed distribution and the fitted one may be due to the rotation of CCl$_4^-$ TNI before getting dissociated.

However, the best fit is for $A_1 + T_1$ fit [Figs. 3 and 4] with the dominant contribution is from $A_1$.