SUPPLEMENTARY INFORMATION for Dissociative electron attachment to carbon tetrachloride probed by velocity map imaging

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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:

$$E_{\rm Th} = D({\rm CCl}_3 - {\rm Cl}) + D({\rm CCl}_2 - {\rm Cl}) - EA({\rm Cl})$$
$$= (3.0 + 3.7 - 3.61) = 3.09 \, {\rm eV}$$

Where, $D(CCl_3-Cl)$, $D(CCl_2-Cl)$, and D(CCl-Cl) are bond dissociation energies (BDEs) of CCl_3-Cl , CCl_2-Cl , and CCl-Cl respectively.

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

$$\begin{split} E_{\rm Th} = & D({\rm CCl}_3 - {\rm Cl}) + D({\rm CCl}_2 - {\rm Cl}) + D({\rm CCl} - {\rm Cl}) \\ & - D({\rm Cl} - {\rm Cl}) - {\rm EA}({\rm Cl}) \\ = & (3.0 + 3.7 + 3.4 - 2.4 - 3.61) = 4.09 \, {\rm eV} \end{split}$$

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

$$\begin{split} E_{\rm Th} = & D({\rm CCl}_3 - {\rm Cl}) + D({\rm CCl}_2 - {\rm Cl}) + D({\rm CCl} - {\rm Cl}) \\ & - {\rm EA}({\rm Cl}) \\ = & (3.0 + 3.7 + 3.4 - 3.61) = 6.49 \, {\rm eV} \end{split}$$

B. Cl_2^- dissociation channels

The threshold energy for channel (a) in Table IV of the main text for the production of Cl_2^- can be estimated using the formula:

$$\begin{split} {\rm E_{Th}} = & {\rm D}({\rm CCl}_3 - {\rm Cl}) + {\rm D}({\rm CCl}_2 - {\rm Cl}) - {\rm D}({\rm Cl} - {\rm Cl}) \\ & - {\rm EA}({\rm Cl}_2) \\ = & (3.0 + 3.7 - 2.4 - 2.9) = 1.4 \, {\rm eV} \end{split}$$

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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:

$$\begin{split} \mathbf{E}_{\mathrm{Th}} = & \mathbf{D}(\mathrm{CCl}_3 - \mathrm{Cl}) + \mathbf{D}(\mathrm{CCl}_2 - \mathrm{Cl}) - \mathbf{D}(\mathrm{Cl} - \mathrm{Cl}) \\ & - \mathrm{EA}(\mathrm{Cl}_2) + \mathbf{D}(\mathrm{CCl} - \mathrm{Cl}) \\ = & (3.0 + 3.7 - 2.4 - 2.9 + 3.4) = 4.8 \, \mathrm{eV} \end{split}$$

C. CCl_2^- dissociation channels

The threshold energy in Table V of the main text for channel (a) for the production of CCl_2^- can be estimated using the formula:

$$\begin{split} \mathbf{E}_{\mathrm{Th}} = & \mathbf{D}(\mathrm{CCl}_3 - \mathrm{Cl}) + \mathbf{D}(\mathrm{CCl}_2 - \mathrm{Cl}) - \mathrm{EA}(\mathrm{CCl}_2) \\ = & (3.0 + 3.7 - 1.8) = 4.9 \, \mathrm{eV} \end{split}$$

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

$$\begin{split} {\rm E_{Th}} = & {\rm D}({\rm CCl}_3 - {\rm Cl}) + {\rm D}({\rm CCl}_2 - {\rm Cl}) - {\rm D}({\rm Cl} - {\rm Cl}) \\ & - {\rm EA}({\rm CCl}_2) \\ = & (3.0 + 3.7 - 2.4 - 1.8) = 2.5 \, {\rm eV} \end{split}$$

II. ANALYSIS OF ANGULAR DISTRIBUTIONS OF CL_2^- AND CCL_2^- 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:

$$I(\theta,\phi,k) = \sum_{\mu} |\sum_{l=\mu} a_{l\mu}(k) Y_l^{\mu}(\theta,\phi) e^{i\delta_l}|^2$$
(1)

where $a_{l\mu}(k)$ are energy-dependent expansion coefficients, k is the incident electron momentum, $Y_l^{\mu}(\theta, \phi)$ are the spherical harmonics, μ 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 (θ, ϕ) are the polar angles of the negative ion fragments with respect to the incident electron direction.

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FIG. 1. Angular Distribution of Cl_2^- ions having kinetic energy ≥ 0.6 eV, arising from the DEA to CCl_4 at 6.0 eV incident electron energy. The solid blue lines represents the fit with (a) A_1 (b) T_1 , (c) E and (d) T_2 resonant symmetry considering only the the direct bond breaking.



FIG. 2. Angular Distribution of CCl_2^- ions arising from the DEA to CCl_4 at 6.0 eV incident electron energy. The solid blue lines represents the fit with (a) A_1 (b) T_1 , (c) E and (d) T_2 resonant symmetry considering only the the direct bond breaking.

Later Azaria *et al.* [2] extrapolated the expression for polyatomic molecules and found the angular distribution of the negative ion fragments averaging over ϕ . The expression is as follows:

$$I(\theta) = \frac{1}{2\pi} \int_0^{2\pi} |\sum_{l\mu\epsilon} i^l e^{i\delta_l} a^{\epsilon}_{l\mu} X^{\epsilon}_{l\mu}(\theta,\phi)|^2 d\phi \qquad (2)$$

where $X_{l\mu}^{\epsilon}$ are the basis functions for the irreducible rep-

resentation	of the	he	group	of t	the m	olec	ule,	$a_{l\mu}^{\epsilon}$	are	t]	heir
amplitude a	and a	all	other	varia	ables	are	${\rm the}$	sam	e a	\mathbf{s}	dis-
cussed earlie	er.										

Irreducible	Basis functions
representations	
	$Y_0^0; l = 0, 1$
A_1	Y_3^{-2} ; $l = 3$
	$\left(\sqrt{\frac{5}{12}}\mathbf{Y}_{4}^{4}+\sqrt{\frac{7}{12}}\mathbf{Y}_{4}^{0}\right); l=4$
A_2	-
Е	$(Y_2^0, Y_2^2); l = 2$
	$(Y_4^2, \sqrt{\frac{5}{12}}Y_4^4 - \sqrt{\frac{7}{12}}Y_4^0); l = 4$
T_1	$\left(\sqrt{\frac{3}{8}}Y_3^3 + \sqrt{\frac{5}{8}}Y_3^1, Y_3^2, -\sqrt{\frac{3}{8}}Y_3^{-3} + \sqrt{\frac{5}{8}}Y_3^{-1}\right)$
	$(\sqrt{\frac{1}{8}}Y_4^{-3} + \sqrt{\frac{7}{8}}Y_4^{-1}, Y_4^{-4},$
	$-\sqrt{\frac{1}{8}}Y_4^3 + \sqrt{\frac{7}{8}}Y_4^1)$
	(Y_1^1, Y_1^0, Y_1^{-1})
T_2	$(Y_2^{-1}, Y_2^{-2}, Y_2^{-1})$
	$\left(\sqrt{\frac{5}{8}}Y_3^3 - \sqrt{\frac{3}{8}}Y_3^1, Y_3^0, -\sqrt{\frac{5}{8}}Y_3^{-3} - \sqrt{\frac{3}{8}}Y_3^{-1}\right)$

TABLE I. Character table of T_d point group and basis functions [3].

The basis functions for different states with different symmetries for molecules with T_d point group symmetry are listed in table I. There are five irreducible representations A_1 , A_2 , E, T_1 , and T_2 under the T_d point group symmetry. Different electronic states, therefore, can be represented as these irreducible representations. The A_1 and A_2 are two non-degenerate irreducible representations, while E is the doubly degenerate one. On the other hand, T_1 and T_2 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 Cl_2^- and CCl_2^- 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 Esymmetry. 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 forwardbackward asymmetry.

The blue solid curve in Fig. 1 (c) and 2 (c) represents the best fit with E resonant symmetry under the T_d point group symmetry considering the axial recoil approximation for Cl_2^- and CCl_2^- ions respectively. Under this approximation, the ejection directions of both the Cl_2^- and CCl_2^- 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 = $109^{\circ}/2 = 54.75^{\circ}$ with the C–Cl bond]. For the fitting, we have considered only the d-partial wave (l = 2). This suggests that most of the Cl_2^- 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 CCl_2^- ions.



FIG. 3. The solid blue line represents the fit with the combination of A_1 and T_1 resonant symmetry considering axial recoil approximation.

The Vacuum Ultraviolet (VUV) absorption spectra of CCl_4 on the other hand, suggests the presence of $n \to \sigma^*$ ($2t_1 \to 7a_1$) 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) $2t_1^5$ $7a_1^2$ with T_1 symmetry. In Figs. 1 (b) and 2 (b), we have shown the fit to the angular distribution of Cl_2^- and CCl_2^- ions respectively with T_1 resonant symmetry considering the simple direct bond breaking approximation.



FIG. 4. The solid blue line represents the fit with the combination of A_1 and T_1 resonant symmetry considering axial recoil approximation.

Although the fit with T_1 symmetry can justify the forward-backward asymmetry, the interference between

the f and g partial waves produces this asymmetry. However, the fit for the direct bond-breaking model can not explain the distribution completely. Also, the effect of the rotation of the CCl₄ TNI before getting dissociated can not 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 CCl₄ TNI.

From Figs. 1 (a)-(d), it can be seen that the best fit to the angular distribution of Cl_2^- ions is for A_1 resonant

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symmetry under axial recoil approximation. This is also the case for CCl_2^- ions [Figs. 2 (a)-(d)].

Although it can not 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 .

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