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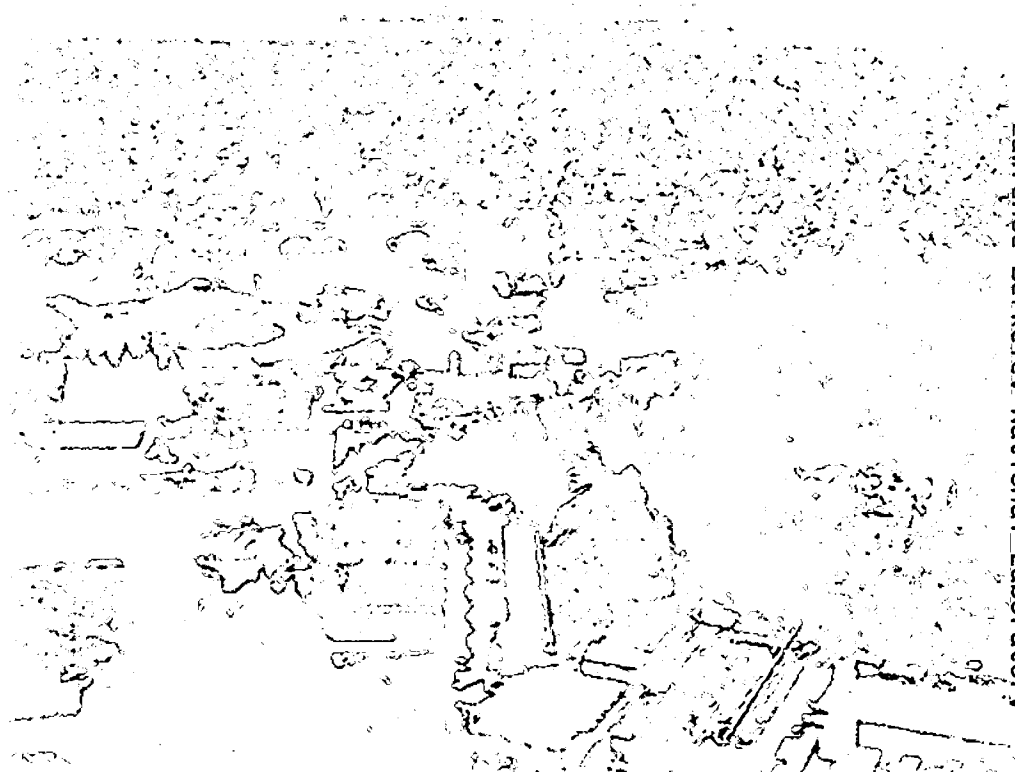
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**Evidence of Triplet Ethylene Produced from
Photodissociation of Ethylene Sulfide**

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Abstract

Tunable synchrotron radiation has been used to probe the dissociation dynamics of ethylene sulfide, providing selective determination of the translational energy distributions of both excited (1D) and ground state (3P) sulfur atoms, with momentum-matching to the ethylene cofragments. The results suggest the presence of a channel giving S(3P) in conjunction with *triplet* ethylene C₂H₄ ($^3B_{1u}$), and allow for the first experimental measure of the energy of the latter species near the equilibrium geometry, in which the two methylene groups occupy perpendicular planes.

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Ethylene is a molecule of broad fundamental and practical importance. It is a central species in hydrocarbon combustion and in interstellar chemistry; a key hormone in biological systems, and a synthetic precursor to vast array of commercial products¹⁻⁵. As the simplest unsaturated system, its electronic structure and spectroscopy have challenged theorists since the early work of Mulliken^{6,7}. Although the properties of the ground state molecule are well understood, experimental insight into the equilibrium properties of the lowest excited states is lacking owing to dramatically differing geometries for the ground and excited states (Fig. 1). The ground electronic state of the molecule is the familiar singlet, planar species (¹A_g). Promotion of one of the bonding π electrons to an antibonding π^* orbital, with a concomitant change of spin, gives the lowest triplet species (³B_{1u}). The tremendous geometry change accompanying this transition means that, even for non-optical probe techniques such as electron scattering that are sensitive to the spin-forbidden transition⁸⁻¹⁰, the vanishing overlap of the vibrational wave functions for the two species precludes insight into the properties of the triplet molecule near its equilibrium geometry. Photodissociation, however, may give rise to triplet ethylene directly in the vicinity of its equilibrium geometry. Measurement of the translational energy distributions for a photodissociation event that yields the triplet species can thus be used to obtain important energetic and structural information, if this component of the photochemistry can be uniquely identified. We here report the use of tunable synchrotron undulator radiation on the Chemical Dynamics Beamline of the Advanced Light Source, to probe selectively the singlet and triplet sulfur atom products of the photodissociation of ethylene sulfide at 193 nm. Our results indicate the presence of a channel producing triplet C₂H₄ (³B_{1u}), and provide the first experimental insight into the energetics of this species near its equilibrium geometry.

The electronic spectrum of ethylene sulfide shows a number of sharp peaks, with the intense absorption near 193nm assigned to the $4p\pi \leftarrow 3p\pi$ Rydberg transition¹¹. Previous photodissociation studies of ethylene sulfide at 193 nm have shown the importance of a process yielding electronically excited sulfur atoms (¹D) and the ground electronic state (¹A_g) of ethylene, using both photofragment translational spectroscopy (PTS)¹² and Doppler spectroscopy via laser induced fluorescence¹³. In addition, the PTS experiments identified additional channels yielding SH + C₂H₃, and H + SC₂H₃. We

have studied this problem using PTS, but with product detection employing soft photoionization using vacuum ultraviolet (VUV) light rather than electron impact ionization, allowing us to identify additional channels not apparent in the previous work.

Our experiments were performed on beamline 9.0.2.1 of the Advanced Light Source using a rotatable source molecular beam apparatus described in detail elsewhere¹⁴⁻¹⁷. A molecular beam of 10% ethylene sulfide seeded in helium was expanded from a pulsed valve and skimmed twice before entering into the main chamber where it was intersected at 90° by an ArF excimer laser beam. A small fraction of the photofragments entered an aperture into a triply differentially pumped detector region and were photoionized 15.2 cm from the interaction region using tunable vacuum ultraviolet synchrotron undulator radiation (10^{16} photons/sec; $\Delta E/E=2.2\%$). The resulting ions were mass selected by a quadrupole mass filter and counted with a Daly ion counter as a function of flight time and scattering angle. Care was taken to ensure that the TOF spectra shown here are free of multiphoton effects. The tunability of the VUV light source allows for the selective ionization of products with very low background counts. A gas filter was filled with about 25 Torr Ar to eliminate higher harmonics of the undulator radiation. In measuring TOF spectra of sulfur atoms, a MgF₂ optical filter also was used to eliminate small contamination of the probe light by higher energy photons.

TOF spectra of photofragments from photodissociation of *c*-C₂H₄S at 193 nm were measured at several angles (between the molecular beam and detector axis) from 20° to 50°. Signals at $m/e = 59, 34, 33, 32, 28, 27$ and 26 were detected, corresponding to C₂H₃S, H₂S, HS, S, C₂H₄, C₂H₃ and H₂CC: respectively. In this Communication, however, we focus on the $m/e=32$ and 28 channels. Center-of-mass translational energy distributions, $P(E_T)$ s were obtained by forward-convolution fitting of the recorded TOF spectra¹⁸. Although we show TOF spectra for only one angle for each product, multiple angles were recorded and fitted for each channel.

The use of tunable synchrotron radiation to probe the sulfur atom allows us to distinguish the electronically excited S (¹D) from the ground state (³P) sulfur atom products owing to the fact that the ionization potential for the former is more than 1 eV lower than the latter. This approach has recently been used to unravel the two contributions in the dissociation dynamics for CS₂¹⁹. TOF spectra of $m/e=32$ (S atom)

were measured at the photon energies of 9.5 eV (Fig. 2(a)) and 10.8 eV (Fig. 2(b)) at a scattering angle of 20°. The ionization potential of S is well known to be 9.21 and 10.36 eV for the first electronic excited state 1D and the ground state 3P , respectively²⁰. Hence the TOF spectra of mass 32 at 9.5 eV corresponds exclusively to the contribution of the excited state 1D sulfur atom. It was fitted very well using the translational energy distribution, $P(E_T)$, shown in Fig. 3(a). In fact, this $P(E_T)$ includes three components, broadly peaked at 40, 24, and 5 kcal/mol, respectively. We assign these to dissociation on the initially prepared 1A_1 excited state, and two lower lying states after internal conversion: the 1B_2 excited state and the ground state, respectively. The detailed dynamics of these processes will be discussed in detail in a future publication²¹. The maximum translational energy release extends out to 65 kcal/mol, which is close to the available energy of the $S(^1D) + C_2H_4(^1A_g)$ channel. Therefore, the TOF spectra of mass 32 in Fig. 2(a) corresponds to a production of the excited state (1D) sulfur and the ground state (1A_g) ethylene.

However, the appearance of the TOF spectrum changes dramatically as the photoionization energy is increased to detect the ground state S atom. This TOF spectrum includes both the excited state (1D) discussed above, and a ground state $S(^3P)$ contribution. In addition to the translational energy distribution determined previously for the excited sulfur atom, two more translational energy distributions (Figure 3(b), and 3(c)) were used to fit the TOF spectra of S at 10.8 eV. One, shown in Figure 3(b), fits the high-energy tail, but also shows a peak at low energy. This broad distribution is assigned to the spin-forbidden product channel $S(^3P)+C_2H_4(^1A_g)$. This spin-changing process is not unusual in sulfur-containing compounds, and likely results from intersystem crossing to a triplet surface prior to dissociation. There is an additional feature, however, that arises clearly in the ground state S atom TOF distribution that appears precisely in the energy region where one would expect the spin-conserving dissociation to $S(^3P)+C_2H_4(^3B_{1u})$. This feature was fitted with the $P(E)$ shown in Figure 3(c), peaking at 24 kcal/mol and extending to a maximum at 34 kcal/mol.

The TOF spectrum of $m/e=28$ (ethylene) also was measured at 11 eV, above the ionization potential (10.51 eV) of the ground state ethylene, and is also shown in Fig. 2. The multi-modal structure that is clear in the sulfur atom is also fully reproduced in our

$m/e=28$ TOF spectra. The $m/e=28$ spectrum was fitted with precisely the same $P(E_T)$ s, but with different relative yields of the fast and slow contributions (consistent with different relative photoionization efficiencies). The peak around 45 μsec is assigned to the triplet ethylene. In addition, the photoionization yield of mass 28 was measured by integrating three different parts (Fig. 4) as a function of probe photon energy. The onsets are completely different: the fast part corresponds to the internally cold ethylene with little vibrational excitation; the slow part to the internal "hot" ethylene with considerable vibrational excitation; the middle part to the *triplet* ethylene. It should be borne in mind, however, that intersystem crossing to the ground state ethylene is likely complete during the flight time (40 microseconds) to the detector. The two slower peaks show dramatically red-shifted photoionization yield spectra, consistent with the internal energy inferred for these processes. Although the previous PTS study reported a single TOF peak for m/e 28, this discrepancy is likely attributable to near-complete fragmentation of the slow ethylene component, containing nearly 3 eV internal energy, in the electron bombardment detector in that study.

The contribution of dissociative ionization of larger fragments (H_2S and HS) to our sulfur atom signal can be excluded in this study, since soft photoionization was used. In the previous PTS study, four contributions to the TOF spectra of sulfur atoms were identified, including dissociative ionization of HS and SC_2H_3 , and multiphoton processes, in addition to the process $\text{S}(^1\text{D}) + \text{C}_2\text{H}_4(^1\text{A}_g)$ ¹². These other contributions obscured the contribution from slow primary $\text{S}(^3\text{P})$ in the electron-impact based study. Although Kim et al. reported no evidence of $\text{S}(^3\text{P})$ in the 193nm photodissociation of ethylene sulfide, based on LIF probing, their sensitivity was not explicitly stated. Felder et al. reported fast sulfur atoms, beyond the energetic limit for formation $\text{S}(^1\text{D})$, which must therefore correspond to a spin-forbidden process giving $\text{S}(^3\text{P}) + \text{C}_2\text{H}_4(^1\text{A}_g)$. This result is clearly confirmed in our work, implying significant limits to the sensitivity to the $\text{S}(^3\text{P})$ for the LIF experiment. Furthermore, our result is in good agreement with a velocity map imaging study of 193 nm photodissociation of *c*- $\text{C}_2\text{H}_4\text{S}$ ²². Abundant formation of spin-forbidden fragment pairs has been observed in other sulfur-containing compounds such as CS_2 , and SO_2 ^{19,23,24}.

The $P(E_T)$ in Fig 3(c) implies the production of triplet ethylene near the predicted threshold for its formation based upon ab initio calculations²⁵. This ‘photochemical synthesis’ thus produces a small amount of C_2H_4 ($^3B_{1u}$) near its equilibrium geometry. An upper limit to the heat of formation of C_2H_4 ($^3B_{1u}$) can be inferred from the maximum extent of the translational energy distribution for this channel: a value of 70 ± 3 kcal/mol is obtained, which is 58 ± 3 kcal/mol above the ground state ethylene. This is in good agreement with theoretical predictions: the ground state of ethylene is more stable than the triplet state by 64 kcal/mol at their respective equilibrium geometries²⁵. Theoretical calculations²⁵ and electron energy loss spectroscopy⁹ revealed that the $1^1A_g \rightarrow 1^3B_{1u}$ vertical transition energy (i.e., at the planar geometry of the ground state) occurred at 106 kcal/mol (4.6 eV) and 97 kcal/mol (4.2 eV), respectively. Weiner and coworkers have recently invoked the production of triplet ethylene in a study of the photodissociation of ethylene episulfoxide, $c-C_2H_4SO$, based upon the more favorable agreement they achieve between their measured SO vibrational distributions and those predicted by models of the dissociation dynamics when triplet ethylene is assumed to be the coproduct. Our more direct insight into the analogous process for ethylene sulfide provides strong support for their interpretation.

One haunting feature of the present results is that both the singlet and triplet S atom translational energy distributions show peaks in the vicinity of 24 kcal/mol. At first it may seem odd to assign these to different processes; a moment’s reflection reveals, however, that it is really quite unlikely they could come from the same process, given the substantial difference in electronic energy for the two states of the sulfur atom. As mentioned above, we believe this broad central peak in the $S(^1D)$ $P(E_T)$ most likely arises from dissociation from a second excited state accessed via internal conversion from the initially prepared state. Although a similar explanation is possible for the faster peak in the ground state S atom $P(E_T)$, we think it also quite likely that the initially prepared singlet state could dissociate directly to $S(^3P) + C_2H_4(^3B_{1u})$. In a sense, this means that the 24 kcal/mol feature in the $S(^3P)$ is actually related to the *fastest* feature in the $S(^1D)$ distribution. The fact that the maximum energy of the 24 kcal/mol $S(^3P)$ peak yields an energy of the triplet ethylene species in reasonable agreement with recent theoretical predictions provides further support for our assignment. Although the evidence presented

here for the production of triplet ethylene from ethylene sulfide photodissociation is by no means definitive, we believe this is the most likely explanation for the observations. A definitive experimental answer could be somewhat elusive, but might take the form of time-resolved photoelectron spectra, for example. More detailed theoretical investigations are likely to be the most direct route to further insight into the implications of our observations.

Acknowledgments

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FIGURE CAPTIONS

1. Schematic diagram showing the energy of the ground singlet state and lowest triplet excited state of ethylene as a function of torsion angle, ϕ , adapted from Reference 25.
2. Time-of-flight (TOF) spectra for the S and C₂H₄ channel at the scattering angle of 20° and the indicated probe photon energy. Circles are experimental points, dashed lines are single channel fits to the spectra using the P(E)s in Fig. 3, and the solid line is the total fit to the data.
3. Translational energy distributions (P(E)'s) for the indicated product channels obtained from fits to the data in Figure 2.
4. Photoionization yield of mass 28 at the scattering angle of 20°.

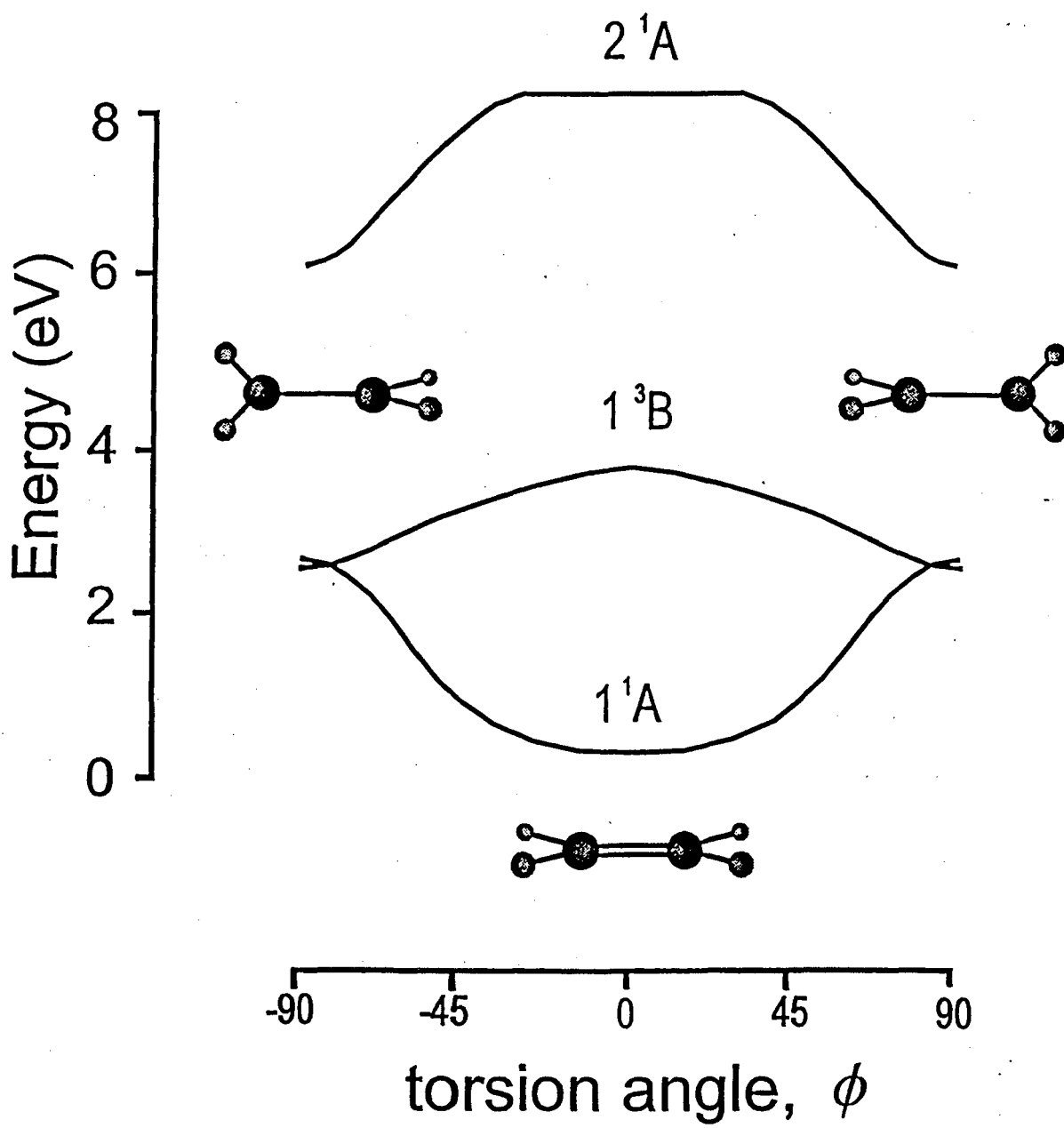


Fig. 1

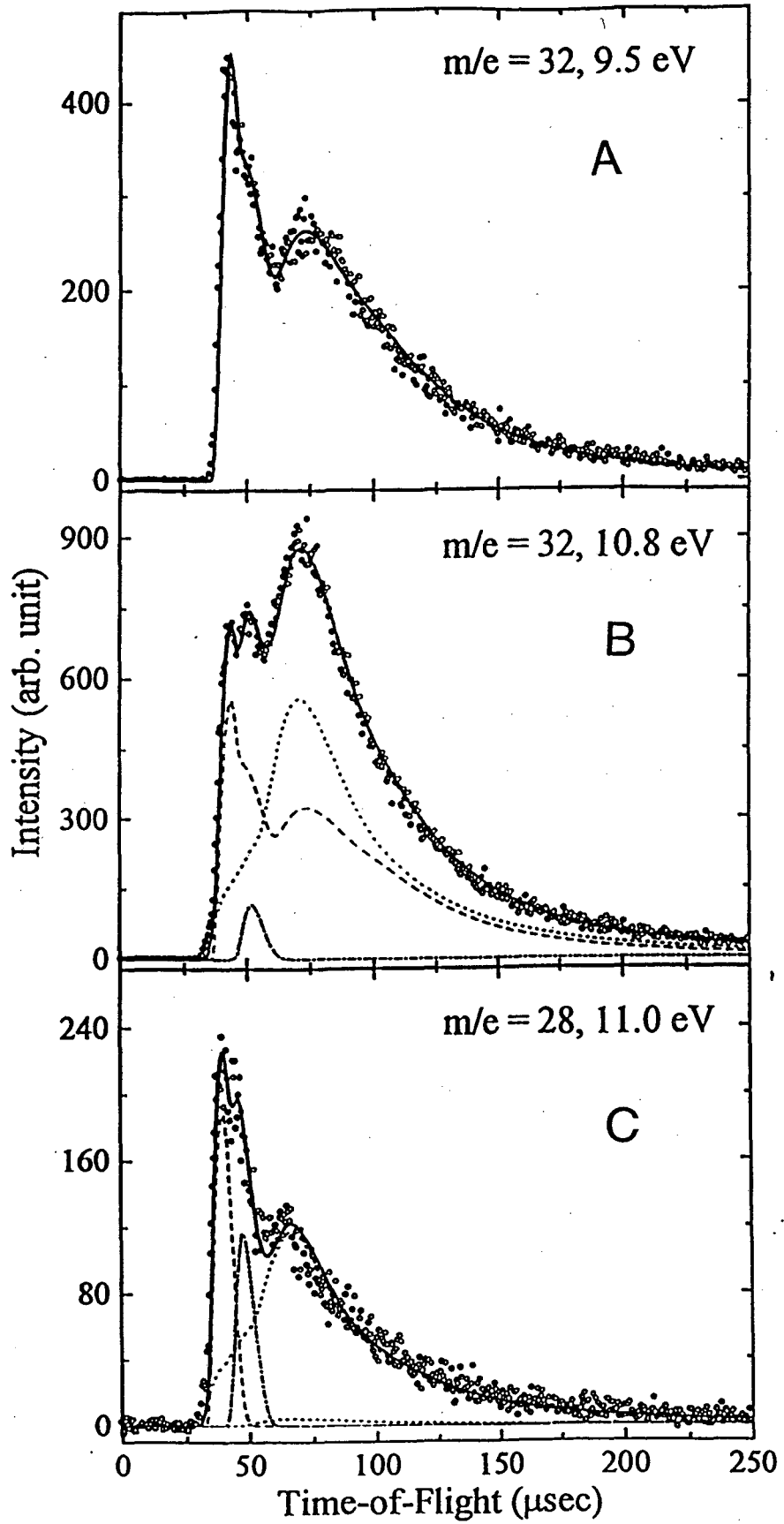


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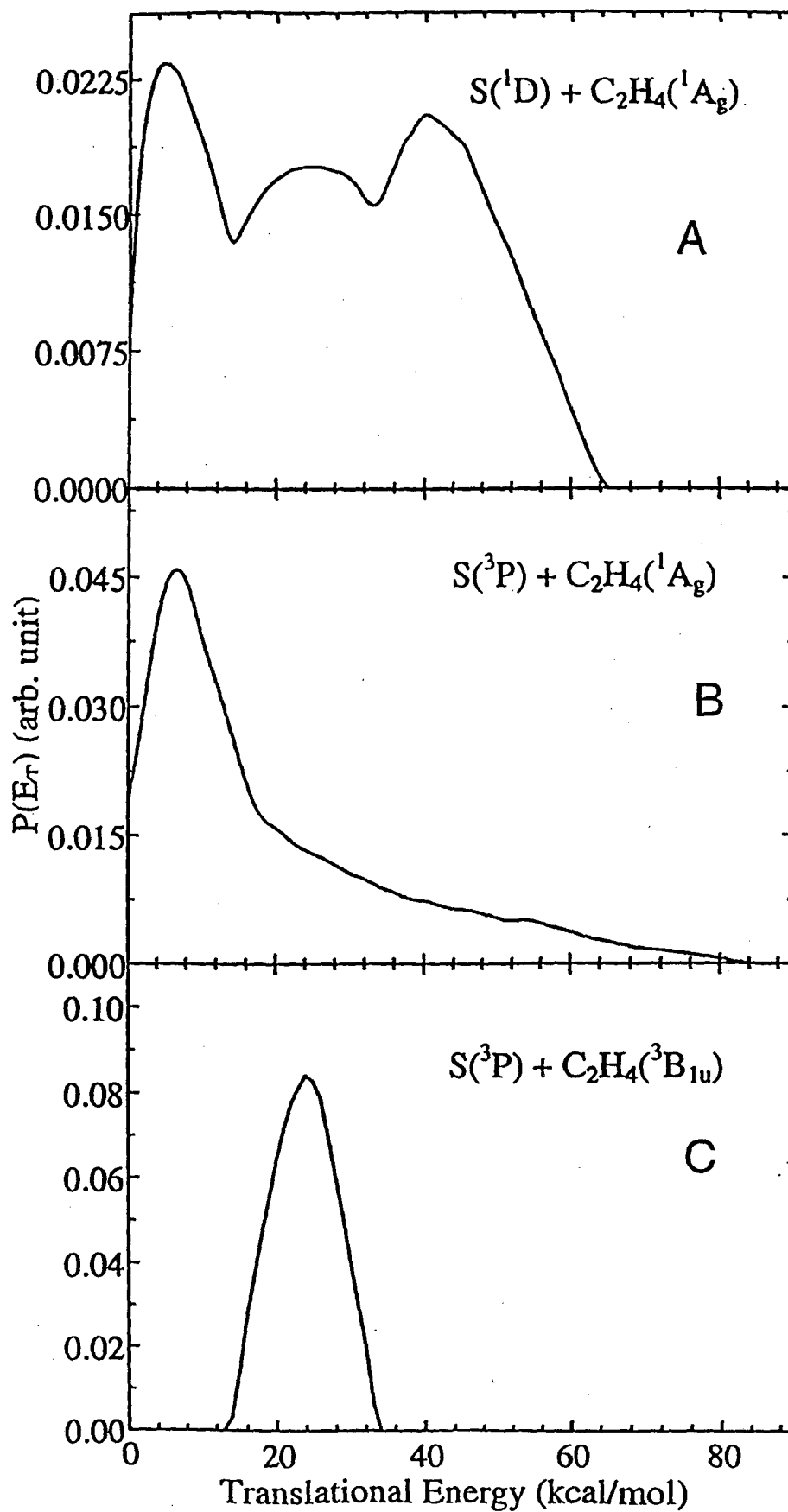


Fig. 3

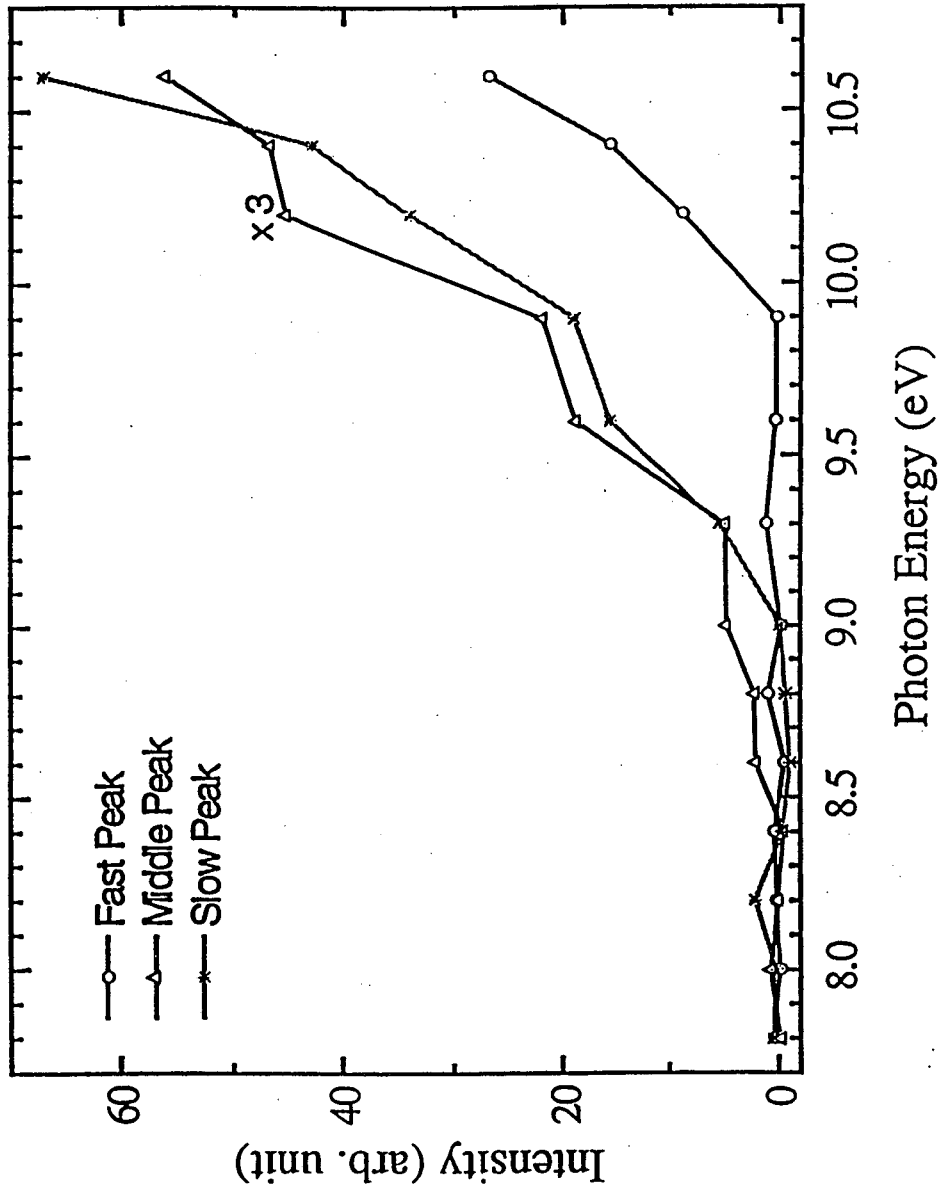


Fig. 4

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