Correlating Parent-Fragment Relationships in Cluster Photoionization

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Fragment signals in ordinary mass spectra carry no label to identify their parent molecule. This complicates the analysis of heterogeneous samples because observed fragments can originate from different parent species. With mass-correlated rotational alignment spectroscopy, we resolved this problem: ion signals obtained through pump-probe photoionization of molecules in a cold molecular beam are correlated with the rotational Raman spectra of their neutral precursors.

Isolated molecular clusters represent a particularly interesting class of heterogeneous molecular samples, because they can serve as model systems for the observation of specific intermolecular interactions and reactions. We investigated a simple molecular beam containing carbon disulfide (CS_2) molecules, its naturally occurring isotopologues, molecular clusters, and sample impurities. In a single data set, we identified 29 distinct ionization and fragmentation channels, revealing a surprising complexity for this rather simple model system.

Fig. 1 shows some spectroscopic results. Rotational spectra correlated with multiple fragment masses (e.g., 12 u, 32 u) show the rotational fingerprint of the most abundant CS_2 isotopologue (76 u), while others show those from heavy parent isotopologues (e.g., 33 u, 34 u due to ^{33}S and ^{34}S containing isotopologues). The CS_2 dimer spectrum is observed in the dimer mass channel (152 u) but also in fragment channels (88 u, 76 u, 64 u).

Our data revealed unexpected dimer fragmentation channels into SCCS and S_2 cations. The formation of these fragments requires the breaking of strong covalent bonds before cluster fragmentation.

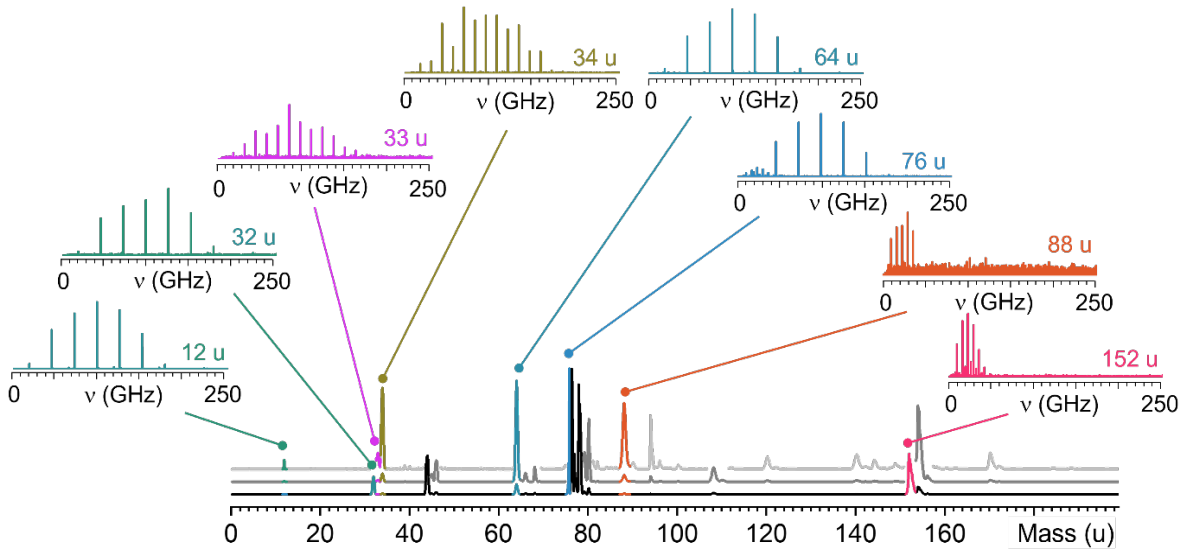

Figure 1: *(Bottom) Photoionization mass spectrum for a cold molecular beam containing CS_2 molecules, naturally occurring isotopologues, and clusters. Grey traces show the same spectrum with 22-fold and 500-fold enlarged ordinate. (Top) Mass-correlated rotational Raman spectra for a few selected mass channels.*