Figure S1. NMR spectrum of crotonaldehyde obtained with a 300 MHz spectrometer.

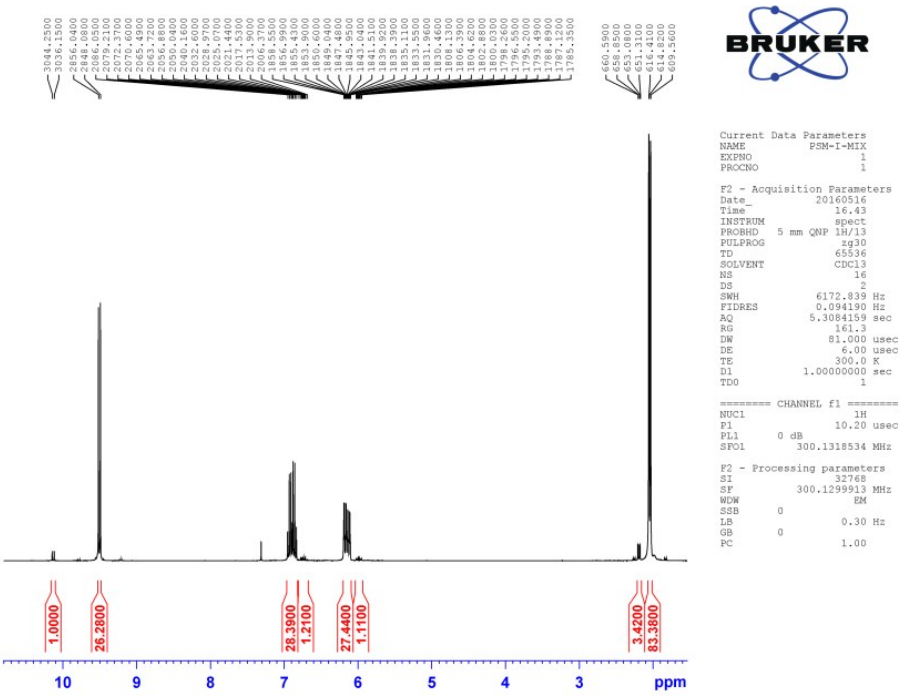

Figure S2. Different stagnation pressures of He and Ar.

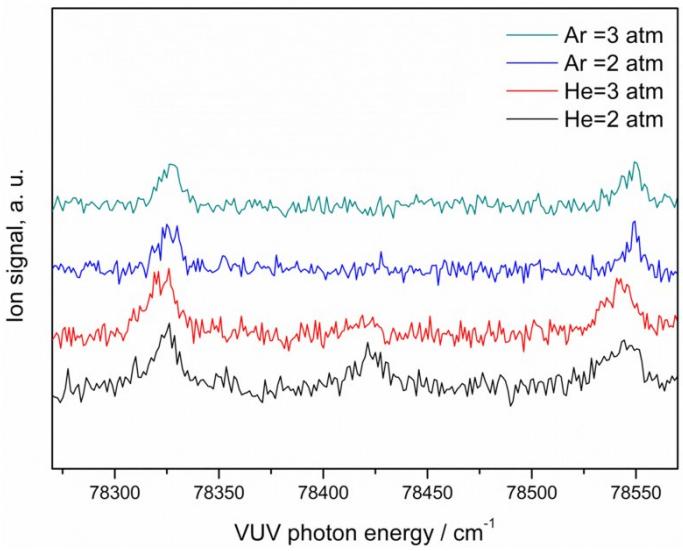

Table S1. Energetics data for crotonaldehyde calculated at various levels.

Level	Isomers	ΔE (S_0)[a]	IE	ΔIE[b]	Level	Isomers	ΔE (S_0)[a]	IE	ΔIE[b]
B3LYP/ cc-pVTZ	tt	0	75,784	0	M062x/aug-cc-pVTZ	tt	0	77,934	0
	ts	674	75,821	38		ts	667	77,997	63
	ct	1071	75,461	-323		ct	1030	77,635	-299
	cc	1280	74,918	-866		cc	1398	77,196	-738
B3LYP/aug-cc-pVTZ	tt	0	76,021	0	ωB97xd/ cc-pVTZ	tt	0	75,938	0
	ts	754	75,986	-35		ts	590	76,070	132
	ct	1070	75,704	-316		ct	948	75,737	-201
	cc	1373	75,028	-993		cc	1154	75,383	-555
B3LYP/aug-cc-pVTZ	tt	0	76,171	0	ωB97xd/aug-cc-pVDZ	tt	0	76,329	0
	ts	767	76,144	-27		ts	649	76,400	70
	ct	1067	75,848	-323		ct	1013	76,034	-296
	cc	1392	75,220	-951		cc	1337	75,565	-764
CAM-B3LYP/ cc-pVTZ	tt	0	76,468	0	ωB97xd/aug-cc-pVTZ	tt	0	76,223	0
	ts	601	76,600	132		ts	693	76,291	68
	ct	1074	76,249	-219		ct	941	75,988	-235
	cc	1230	75,879	-589		cc	1389	75,473	-750
CAM-B3LYP/aug-cc-pVDZ	tt	0	76,688	0	MP2/ cc-pVDZ	tt	0	78,045	0
	ts	695	76,745	58		ts	453	78,460	416
	ct	1071	76,481	-207		ct	1073	78,065	21
	cc	1331	75,986	-701		cc	1045	78,167	122
CAM-B3LYP/aug-cc-pVTZ	tt	0	76,854	0	MP2/aug-cc-pVDZ	tt	0	80,446	0
	ts	712	76,912	58		ts	781	80,717	271
	ct	1069	76,639	-215		ct	1019	80,512	66
	cc	1370	76,161	-694		cc	1359	80,387	-60
M062x/ cc-pVTZ	tt	0	77,675	0	CCSD/ cc-pVDZ	tt	0	74,741	0
	ts	566	77,804	129		ts	386	75,065	324
	ct	915	77,502	-173		ct	1021	74,603	-137
	cc	1287	77,017	-658		cc	1018	74,602	-139
M062x/aug-cc-pVDZ	tt	0	77,430	0					
	ts	634	77,507	77					
	ct	973	77,230	-200					

cc	1386	76,647	-783

[a] Relative energies for the other conformers with respect to that of the trans-s-trans (tt) crotonaldehyde on the S_0 state.

[b] Calculated ionization energies for the other conformers with respect to that of tt conformer.